An-Najah National University

Faculty of Graduate Studies

Technical Feasibility of Applying Cleaner Production Practices in Palestinian Leather Tanning Industry

By

Munya Masoud

Supervisors

Dr. Abdelrahim Abu Safa

Prof. Amer Elhamouz

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This thesis was defended successfully on 13/6/2021and approved by:

Defense Committee Members	**Signature**
– Dr. Abdelrahim Abu Safa / Supervisor	…………………………
– Prof. Amer Elhamouz / Co-Supervisor	…………………………
– Dr. Hasan Sawalha / External Examiner	…………………………
– Dr. Husni Odeh / Enternal Examiner	…………………………

Dedication

I would like to heartily thank all those who supported me throughout my education.

To my beloved mother and father and all my family members.

To my friends who never hesitated to help and left me up whenever I needed them.

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الإقرار

أنا الموقعة أدناه، مقدمة الرسالة التي تحمل العنوان:

Technical Feasibility of Applying Cleaner Production Practices in Palestinian Leather Tanning Industries

أقر بأنّ ما اشتملت عليه هذه الرسالة إنما هو نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وأنّ هذه الرسالة كاملة أو أي جزء منها، لم يُقدم من قبل للحصول على أي لقب أو بحث لدى أي مؤسسة بحثية أخرى.

Declaration

The work provided in this thesis unless otherwise referenced is the researcher own work and has not been submitted elsewhere for any other degree or qualification.

Student's Name:	**اسم الطالب:** منية مسعود
Signature:	**التوقيع:**
Date:	**التاريخ:** 13/6/2021

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Abstract

The main objective of this thesis is to recommend cleaner production practices that can be applied to Palestinian tanneries, after the study and investigation of traditional tanning methods in local plants and testing cleaner production practices to select the most applicable one.

In this research project, a lab-scale tanning drum was constructed to carry out the tanning process, hides were brought from local tanneries after the pickling process, traditional tanning method (as Nablus tannery) was applied on skin/hide samples with the variation of two main factors: chromium concentration and water temperature. The optimum values were chosen based on chromium uptake and leather mechanical quality. In each experiment, the initial and final tanning solutions were analyzed for chromium concentration. The temperature was kept constant in each experiment using a temperature controller and electric heater. The tensile strength of the samples was measured using the standard tensile machine. It was found that the chromium uptake fluctuates as the process temperature changes. the chromium uptake increases as the tanning solution concentration increase. On the other hand, the skin/hide quality increases when increasing chromium concentration in tanning bath, but it decreases as temperature increases. The best results of chromium uptake and skin/hide quality were obtained at 25 °C water temperature, with 5.5 % w/w chromium concentration in water (as traditional method), and 100 % w/w water volume according to skin/hide weight (the half of water volume in traditional method). At this ratio, the chromium uptake was 95.33 %, and the consumed

Chapter One

Introduction

1.1 General Background

The leather and footwear industry in Palestine was served as an important industrial sector, because of its contributions to national production, export, and employment. Within this sector, there were about 1000 companies that employed over 10000 employees, and produced approximately 13 million shoe pairs annually, in the mid-1990s (the height of subcontracting activity). By 2013, the leather and footwear industry had about 230 companies that manufacture footwear and 14 tanneries that had about 10 employees each. Nearly all national production of leather is done by the footwear manufacturing sector. The main goods of the footwear sector are slippers, shoes for children, men, and women, sandals, and bags. The annual productivity in 2013 was 4 million footwear pairs, which is about a 70 % decline compared to the year 2000. This was due to the availability of low-priced and latest modern designs of imported footwear products, which have a special appeal from young customers. Palestinian manufacturers were not able to meet these young customers' needs (International Trade Center et al., 2013).

The leather and footwear production sector start with leather provision from leather processing plants which are responsible for the treatment and processing of animals' skins into processed leathers, then the leathers are tanned to be converted into a stable and not putrefy material. The tanning process could cause air and water contamination with trimmings, chromium, and other by-products. To achieve high efficiency and develop a sustainable industry in the footwear and leather manufacturing sector, many changes should take place, including the development of technical and vocational education and training infrastructure, development of eco-friendly footwear industry, and development of environmental sustainability of tanning processes.

The tanning process is water and chemical-consuming, resulting in high amounts of wastewater, high water pollution, and thus a hazardous chemical sludge. Usually, Chromium recycling is carried out using lime as a precipitation agent. Moreover, the precipitated sludge is dissolved by sulfuric acid to recover the unused chromium. To say nothing off, the procurement of sulfuric acid is prohibited in Palestine. therefore the precipitated sludge is transferred for further treatment to the “Israeli” companies specialized in hazardous waste disposal. Such companies impose high charges for such services. Therefore, this project aims to investigate the technical feasibility of the application of cleaner production instead of traditional processes to reduce waste pollutants.

Cleaner production technique has substantial importance in the environmental concern in developed industrial countries. This involves a fundamental understanding of industrial operations, following up strategies to reduce wastes, and trying to achieve successes in pollution prevention trends that are cost-effective and technically feasible.

Cleaner production is defined by United Nations Environment Program (UNEP 2012) as the continuous application of an integrated and preventative environmental strategy to services, products, and processes to increase efficiency and reduce risks to the environment and humans (Duflou & Kellens, 2014).

Cleaner production is a promising approach for solving environmental problems. Therefore, in this project, a cleaner production option will be chosen to be applied to leather tanning in Palestine.

1.2 Objectives

Main Goal:

To investigate appropriate cleaner production practices that can be applied to Palestinian leather industries.

Specific Objectives:

- To study the effects of the operating tanning conditions including water temperature and chromium concentration on chromium uptake.
- To select the optimum operating tanning conditions that give maximum chromium uptake while preserving leather quality.

1.3 Research Questions

Main Research Question:

What are the most suitable operating conditions for the tanning process according to chromium uptake and leather quality?

Sub-Questions:

- What is the effect of increasing temperature on chromium uptake and leather quality?
- What is the effect of increasing chromium concentration on chromium uptake and leather quality?

Chapter Two

Tanning and Cleaner Production

2.1 Leather Tanning

2.1.1 Leather Processing Definition:

Leather processing includes the work needed to convert the putrescible skin/hide of small animals like goats and sheep, and large animals like horses and cows into indestructible leather for different purposes (Dixit et al., 2015).

2.1.2 Leather Processing Steps:

Leather processing goes through several steps (Piera, 2018), these are:

- **Hides' Storage**
  - When hides arrive at the tanning plant, they are sorted into several groups depending on size, thickness, or quality.
  - Hides' salts are reduced by shaking hides using hands to prepare them for the second stage.
  - The unwanted parts from hides are trimmed using the appropriate shaving technique.
  - Hides after that can be stored until the time of beamhouse operations.

- **Beamhouse Operations**
  - Soaking: hides are soaked to restore the lost water due to the salting process and to remove blood, salt and dirt. Firstly, hides are soaked without chemicals to remove blood, salt, and dirt. Secondly, hides are soaked in an alkaline solution ($9.3 < pH < 9.5$) with wetting agents, sodium carbonate to adjust pH, and antibacterial agents to preserve hides.

- Liming: in this process, hides are treated in an alkaline solution ($12.5 < pH < 13$) to remove hair, interfibrillar proteins, and epidermis. The alkaline solution includes lime, sodium hydrosulfide, and sodium sulfide.
- Fleshing: the adhered organic materials like fat are removed by a mechanical fleshing process. This process can be carried out before or after soaking, after liming, or after pickling.
- De-liming: this is a chemical process to decrease pH (8.0 - 9.0) to remove the lime, and to make hides more receptive to the chemicals that will be added in the upcoming stages. This process uses an acidic salt like ammonium sulfate.
- Bating: hides are exposed to an enzymatic effect to remove pigments and hair roots that remained after the liming process, and to open up the structures of hides.
- Degreasing: aqueous emulsification is added with detergents or solvent extraction to remove the excess fat content in hides. This operation is carried out to avoid the interaction between chrome and fats, if this interaction occurs; insoluble chromium soaps will be formed and they will be extremely difficult to be removed.
- Pickling: hides are treated in a solution containing salt, formic acid, and sulfuric acid to lower pH (2.8-3.0). After this process, the tanning material can be homogeneously distributed on hides in the upcoming tanning process.

- **Tanning Processes**

Tanning materials are added like mineral tanning materials or vegetable tanning materials. These materials form stable bonds in the hides' structure with collagen and give hides a high thermal stability and a stable shape.

Tanning is carried out in an acidic solution with pH (2.8 ~ 3.0) for penetration purposes. The most common tanning agent is chromium sulfate; however, alternatives such as aluminum tanning and vegetable tanning are also vastly used. The final hide that contains chrome after chrome tanning is called wet blue because of its color (light blue). This wet blue hide will not be susceptible to putrefaction because of the establishment of collagen fibers by cross-linking of the tanning agents. The hide after this process will be resistant to mechanical actions and heat increase and very stable.

- Sammying: hides and skins are squeezed between two rollers to minimize the moisture amount.
- Splitting**:** in the case of cowhides, hides are split using a splitting machine into two layers to adjust the hides' thickness depending on its final request.
- Hides' selection: hides are selected depending on their final application.
- Shaving: adjust the thickness of hides by a mechanical process depending on the customer order.
- Trimming: hides are trimmed to get rid of unwanted parts.
- Weight: hides are weighed to have control of them.

- **Re-Tanning Processes**

In this stage, there is a conversion from wet blue hide to crust leather. Mechanical and chemical operations are applied to modify the structural differences between leathers and to add specific properties to obtain a regular structure.

- Wet Back: addition of water to hides for re-moisturizing and removing unnecessary particles.
- Re-Chroming: addition of chrome again to hides. This process is necessary for the final product.
- Neutralization: hides are prepared to pH between 5 and 6, and the free acid that exists on the tanned hides is removed, to make hides resist the boiling and be stable against high temperature.
- Re-tanning: this operation is carried out with a pH between 3.5 and 5.0 to give the regular fullness by filling the loose and soft portions of the leather. Also, to improve and retain uniformity and the feel of the leathers.
- Dyeing: this operation is carried out using a little pigment quantity to give the desired color with consistency over the whole surface of hides. Moreover, dyeing gives a good cover for defects.
- Fat-Liquoring: in this process, the lubrication is carried out for dermal fibers to reform the fat content that was lost in the previous processes, and to provide specific features such as fullness and softness.
- Fixation: this operation is carried out to fix all added chemicals from previous steps and to close the fibers of hides by adding formic acid with a pH between 3.0 and 3.5.
- Piling: hides are unloaded from the drum and piled 24 hours before carrying out the next process.
- Setting out: hides are pressed to reduce the rest of the moisture from 100% to 65-70%. Moreover, the grain of hides is flattened and hides are widened.

- Drying: hides are dried using overhead drying and/or vacuum drying to reduce the moisture content from 70% to 20-22%. After that, it is obtained as "crust leather" for the finishing operations.

- **Finishing Processes**

Finishing operations are applied to improve the appearance of the leather (softness, elasticity, and feel), and to provide the expected characteristics of the finished leather. This stage covers different mechanical operations that hide passes to attain the final customer requests like thickness, color, and grain. This stage involves the following mechanical operations:

- Staking: a mechanical operation that is carried out to stretch and soften the leather. Usually, vibrator staking is used, however rotary staking is performed with goats' hides to make them softer.
- Buffing: An optional operation where leather is abraded and the dust that resulted from abrasion is removed from the surface, to obtain a soft and opaque leather surface.
- Spray: an optional operation that is carried out to spray the leather.
- Embossing or ironing: these are mechanical operations, one of them is carried out depending on grain appearance and leather quality. Embossing is carried out in hides of low quality to hide the defects that they have, for example, the final product could be military shoes. In contrast, the ironing process is carried out to hides of high quality to make them smooth.
- Selection and trimmings: the final leathers are separated by grade, size, and thickness, then they are trimmed to obtain appropriate leathers. This process is carried out sometimes just when necessary, not always.

– Measuring and packaging: in this last stage, the area of the leather is measured, packed, and then prepared for export.

Leather processing in Palestine could be summarized as in figure (2.1):

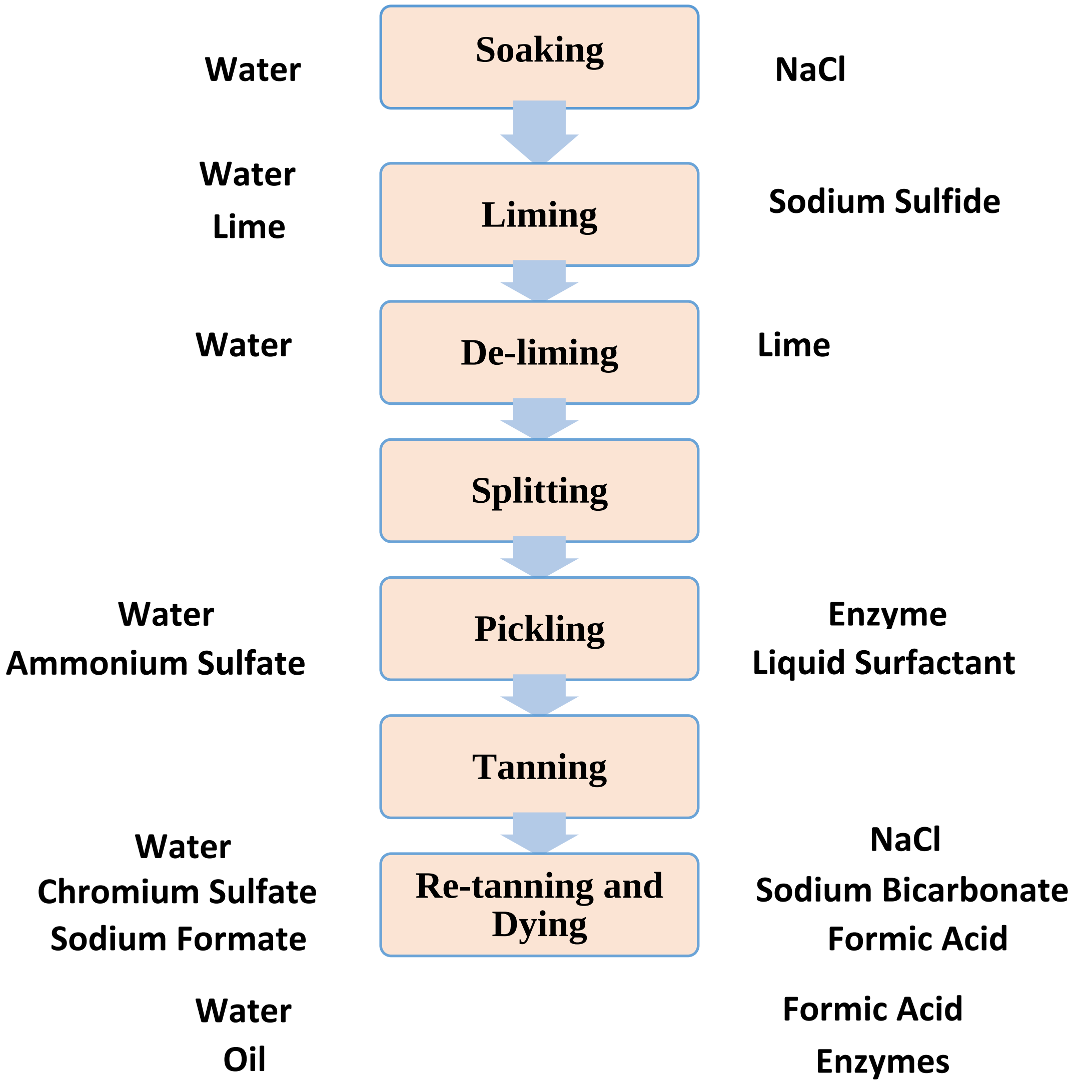

Figure (2.1): Flow Chart for Leather Processing in Palestine

2.1.3 Environmental Pollution from Leather Tanning Processes:

The disposal of wastewater and solid waste containing chromium is a major environmental problem because chromium is an extremely toxic compound, and it's landfilling in many countries is limited to a few specific dumping areas, thus, the minimization of chromium discharge is very important. Air emissions for the tanneries are mostly related to the use of energy. Moreover, the use of organic solvents and dyes causes air emissions. On the other hand, one-fifth of raw hides converted into processed leathers are ready to use in the manufacturing of products such as shoes and sweaters, and the rest of the raw hides remain as waste such as fat, soluble protein, and hair. Also, some parts of hides are shaved or trimmed to form the desired shape and thickness of the leather. Some chemicals also may form a source of waste, such as the used sulfide of unhairing and the used chrome for tanning. In addition, there are micro-pollutants like insecticides that are used for raw stock. All of the mentioned wastes are of growing concern (Mhlanga et al., 2013).

Wastewater is categorized depending on the contaminants that are oxygen demanding, algae promoting, infectious, toxic, or simply unsightly. Wastewater is made up of microorganisms, solids, organic and inorganic substances. The representative constituents and their bad impacts are shown below (Mhlanga et al., 2013):

– Solids: These can be leather trimmings, shavings, cutting, and fleshing residues, hair residues, paper bags remnant. Also, there may be suspended solids in wastewater.
– Oxygen demand: chemical oxygen demand (COD) and biochemical oxygen demand (BOD).
– Nitrogen: total Kjeldahl nitrogen, ammonia, and nitrogen found in proteinaceous materials (from liming/unhairing processes).
– Sulfide: Tannery effluent includes sulfide content from the utilize of sodium hydrosulfide and sodium sulfide that is used in the disposal of hair in the unhairing operation.
– Neutral salts: Chlorides and sulfates.
– Oils and grease

– Chromium compounds

❖ Trivalent chrome (chrome III): Chrome is typically found in wastewater from the tanning process; it is a part of the leather processing, also the chrome comes from the retaining process. Chrome is removed during dyeing and retaining operations.

❖ Hexavalent chrome (chrome VI).

– Other metals such as aluminum and zirconium.

2.2 Cleaner Production

2.2.1 Cleaner Production Definition:

Cleaner production is defined by United Nations Environment Program (UNEP 2012) as the continuous application of an integrated and preventative environmental strategy to services, products, and processes to increase efficiency and reduce risks to the environment and humans (Duflou & Kellens, 2014).

The implementation of cleaner production strategies results on (Cabello-Eras, 2016):

– Pollution prevention.
– Recovery of investment cost.
– Reduction of production cost.
– Cost reduction of wastewater treatment.
– Decreasing water consumption.
– Decreasing energy consumption.
– Decreasing raw materials consumption.
– Minimizing residue generation.

2.2.2 Cleaner Production Strategies:

Based on (Nilson et al., 2007), cleaner production includes one or more of these strategies:

- Products Modification: changing product specifications to be conceivable to minimize waste generation.
- Technology Modification: changing processes and equipment to minimize waste generation.
- Input Substitution: changing input materials to minimize waste generation.
- Good Housekeeping: improving equipment operation and maintenance to minimize waste generation.
- Recycling: reusing the valuable components of the waste stream as input materials for the intermediate or final product.

2.2.3 Prerequisite Factors for Cleaner Production:

As indicated by (Shah et al., 2012), there are prerequisite factors for cleaner production as follows:

- Champion: a successful cleaner production campaign requires a champion in the management, the team that leads and implements cleaner production practices should be comprised of external consultants, company experts, and representatives from engineering, shop floor, and finance. The campaign should make rewards, stimulants, and ratings to encourage the employees to suggest and implement cleaner production practices in the process. It is very important to make clear communication between the company, employees, and community.

- Data: key information for cleaner production should be collected and reported such as water and energy data. The cleaner production strategy requires tracks units for consumption and units' set to make performance measures. The measurements of water and energy should be treated as separate elements, and not rolled into capital operating costs. The successful systems must test performance within goals in regular reports that are viewed by major executives with decision-makers. The operating checklists manual and project data must be provided to the workers in the company. The simple information report is not enough, it is needed to encourage the workers through effective programs for specific and direct information. Therefore, the leaders do not need only information for performance, but also they need to have practical paths through which they can behave. Moreover, the leaders have to know to whom they will contact if there is a lagging facility or another processing unit. The programs for cleaner production should not treat data gathering and reports as a compliance requirement only. Instead of that, they benefit from the cultural ethics of uninterrupted development and improvement, using reporting as a method that helps people to search for new efficiencies and related innovations.

2.2.4 Cleaner Production in Leather Processing:

There are basic environmental issues in leather processing that should be considered when applying cleaner production practices (Crow, 2009), including:

- **Chemicals:** the leather treatment requires wide use of chemicals to clean, treat, and soften hides. The chemicals move into the plant's wastewater and could move into other community water sources and contaminate them. When chemicals are used in a wrong or inefficient way, then production cost and pollution will be increased. The effective chemicals' use can help in pollution reduction and production cost saving.

Selected mitigation strategies for chemicals’ use:

- Development of production operations to increase production efficiency: rising of temperature in chrome baths to increase the chromium adhere to hides, and to reduce the amount of the chemicals that remains in the wastewater. The workers should be instructed about the accurate chemicals' amount to use in tanning and re-tanning processes. Accurate devices should be used to measure the chemicals' amounts to avoid overdosing.
- Improvement of chemicals' storage to avoid leakage and spills. Store chemicals in waterproof and strong containers. The employees should seal the containers well after using them to prevent spills.
- Trying to use safe or less hazardous chemicals as alternatives to hazardous chemicals. For example, the substitution of chromium tanning by vegetable tanning. On the other hand, the quality of leather should be taken into consideration when switching from high polluting chemicals to low polluting chemicals. For instance, the leathers that are tanned by vegetable tanning may have unpredictable colors.
- Recycling of chromium baths from tanning and re-tanning processes. Effluents from chromium and lime could be reused in future production stages when using a filtration system to get rid of solid wastes and get the solution that can be used again. Before the application of such strategies, economic feasibility should be assessed. For instance, recycling chromium baths could be not economically feasible for small processes.

  - **Water use:** the leather treatment requires a huge amount of water because water is needed for each process in leather processing. However, some of the processes or machines can lead to water overuse. Some plants use a pump or well water, this may result in excessive use of water, minimizing of water sources for community use or future production, increasing of energy cost for water pumping, environmental effects due to energy consumption, and lowering of the water table and the need to drill new wells. Moreover, untreated effluents from leather processing may have organic waste that can contaminate sources of local water and decay of water quality in the downstream society. Using water more efficiently will save production costs and prevent water shortages that could cut off production.

Selected mitigation strategies for water use:

- Reuse of water baths from "cleaner" processes of production operation in the "dirtier" process of the next production operation. For instance, using rinsing water from the last process of production for washing or soaking of the next production cycle of other hides.
- Improvement of production ways to conserve water. Shut off water when transfer hides between baths, and between batches. Raising the effectiveness of water spraying by reducing water usage by the installation of nozzles on water hoses. Water levels monitoring or installing of an automatic turn-off technique to avoid water overflowing from baths.
- Use of dry-cleaning methods: swab spills with dry cloths, use cloth or sweepers to remove solid waste from the ground, or by machines before cleaning the ground with water.
- Separation of organic effluent from water bodies.

- **Worker health hazards:** some working conditions in the leather processing industry could be dangerous to workers, such as exposure to chemical materials in processes baths or the air. These situations may result in breathing problems, skin irritations, and dizziness. The workers that have health problems from hazardous working conditions may provide less productive work, cause higher cost, and miss work too often.

Selected mitigation strategies for worker health hazards:

– Use of safety tools for workers such as rubber gloves, safety boots, and facemasks. These small safety improvements can increase productivity in the long run and workers' safety.
– Effective ventilation system in production areas because most of the organic solvents are dangerous when breathed. This exposure can danger workers' health in the long term.
– Training of workers on the appropriate handling of chemical materials. Reduction of chemicals' spills and exposure by instructing workers to follow safety standards. For instance, closing of chemicals' containers when they are not in use to avoid leakage and evaporation. This will help with workers' safety and costs reduction.

- **Odor:** nearly all leather processing baths contain high odorous waste. These strong odors can harm the life quality around the leather processing plants and may damage the community support for more production or expansion. Minimizing odors using waste treatment practices, or waste recycling can enhance community relations and minimize cost.

Selected mitigation strategies for odors' control:

– Separation of non-contaminated wastes and sell to farmers. The untanned residues and fats can be used as agricultural fertilizers if not contaminated with chemicals although they have bad odors.

- Establish a waste treatment or disposal system. Avoid solid waste dumping and use an appropriate landfill or make a pit with a suitable size. Landfilling of wastes will reduce odors. Make sure to dispose of wastes away from water resources.
- Prevent sludge odor by placing it in the treatment area or the landfill. Do not leave the sludge in or around the leather processing plant. Try to dry the standing pools continuously to avoid bad smells from them, and to prevent insects from breeding, especially mosquitoes.

  - **Excess waste:** weak and inefficient production ways result in costly product loss and too much waste generation. Tanning plants that have low-quality production operations may need to rework on a significant proportion of defective products or even dispose of them. Development of production through training and maintenance will save the cost of reworking, minimize products' cost, and reduce environmental effects.

Selected mitigation strategies for excess waste:

- Follow up schedules of regular maintenance for machines. For instance, employees should clean screens and filters of machines that are used in hides' shaving and dehairing regularly to minimize losses or spoilage.
- Use the proper equipment for the production process and train workers on how to use equipment properly as well to perform regular maintenance on such equipment.
- Improve efficiency by identifying opportunities. For instance, use appropriate amounts of hides in the bath, i.e., do not underfill or overfill the baths. Underfilling will waste valuable inputs and overfilling will reduce efficiency.

Chapter Three

Literature Review

In the literature, several types of research were carried out about applying cleaner production strategies to the leather tanning industry, the following is a summary:

(Madanhire & Mbohwa, 2015) studied methods to optimize the usage of chemicals and energy to reduce chemicals' waste generation in the tannery, and to reduce energy. It was observed that leather processing requires accurate quantities of chemicals, and documented work procedures to avoid overdosing and affecting product quality. It was recommended to specialize a well-ventilated place to prepare and mix chemicals; to avoid leakage and pollution. Also, it was recommended to use a pH meter instead of pH paper for better monitoring of acidity for tanning. Moreover, it was suggested to use solar energy instead of electric one to avoid product damage due to power cuts. In the end, the researcher discussed the alternatives of chromium tanning such as vegetable, Aluminum, Titanium, and Zirconium tanning.

(Jian et al., 2012) studied the distribution of chromium in wastewater from tanning and post tanning processes, wastewater from each process was characterized and the chromium content in leather was measured. The results showed that 60% of added chromium is released into wastewater. It was recommended to develop a technique to improve the interaction between collagen and chromium, replacement of re-chroming by another free-chromium pre-tanning process. wastewater collection from the tanning process to recover chromium to be used in post tanning processes; and to reduce chromium content in the effluent and the sludge were also recommended.

(Piera, 2018) analyzed the recent status of solid waste management in the Sheba leather plant to suggest more options that could be important for the environment. The generated wastes were physiochemically characterized and the ability to use part of solid wastes in composting was tested. Also, the decomposition of the raw materials was monitored, and it was found that the decomposition was better without hair. A composting plant was established to treat free-chromium solid waste, this plant consists of a reception/mixing unit, deposit for leachate, and piles unit that needs to be periodically turned and water. This option is an environmentally friendly solution to benefit from part of solid wastes.

(Dandira & Madanhire, 2013) studied the environmental pollution problems from all processes in the leather tanning industry; it was focused on reducing salts and water recycling. It was found that chromium and lime effluent can be used in the next stages without loss of effectiveness; after filtration from suspended solids. Moreover, it was recommended to install a chiller unit to decrease the quantity of used salt in the tannery to 40-50% on skin/hide weight, thus needed water for soaking will be reduced by 30-45%.

(Mhlanga et al., 2013) studied methods for mitigation of environmental risks and increasing the efficiency of leather tanning processing. The chromium tanning was compared with glutaraldehyde tanning with organic agents and syntans. It was found that the physical characteristics of glutaraldehyde tanned leather are better than chromium tanned leather, and by comparing the characteristics of wastewater from both methods, it was found that total solids and chloride are much less in glutaraldehyde tanning. Therefore, glutaraldehyde tanning is more environmentally acceptable than chromium tanning. Moreover, to improve the efficiency of chromium tanning, it was suggested to use a chromium recovery technique by precipitation with magnesium oxide, settling of the suspension, decantation of the supernatant, and subsequent acidification of the precipitate. The experience proved that leather could be tanned using 30% of recovered chromium and 70% of fresh chromium.

(Nashy & Eid, 2019) studied the impacts of chromium tanning effluent to suggest treatment options. It was focused on using two reducing agents "Sodium Bisulfite & Sodium Thiosulfate" with hydroxyl-carboxylic acids and/or basifying agents in the leather tanning process. It was found that Magnesium oxide is the best basifying agent, and Tartaric acid is the best modifying agent. Moreover, if Tartaric acid is followed by Magnesium oxide, in the presence of a reducing agent as Sodium Bisulfite or Sodium Thiosulfate, the best chromium fixation, exhaustion, and shrinkage temperature will be obtained. Also, it was found that the tanning temperature should not exceed 35 °C.

(Fuck et al., 2011) studied the influence of chromium supplied by tanning and wet finishing processes on the formation of Cr(VI) in leather. The influence of Cr (III) from tanning, fat liquors, de-acidification pH, vegetable re-tanning, and chrome re-tanning on the formation of Cr (VI) in leather was analyzed by comparing aged and natural samples. The qualitative and quantitative method of detecting the concentration of Cr(VI) in leather was performed. The results showed that the increase of chromium during tanning and re-tanning will increase the formation of Cr(VI), the type of used oil has an important concern in chromium oxidation, and when pH is 5.5, the formation of Cr(VI) will increase, so it is better to have pH of 4.5 or less. It was recommended to control the oxidizing agents carefully.

(Basaran et al., 2008) studied the distribution of Cr(III) and Cr (VI) in chromium tanned leather. Various concentrations of chromium sulfate were used in tanning and re-tanning processes according to a common recipe, and the amount of hexavalent chromium and chromium oxide was studied in the leather's cross-section. It was found that hexavalent chromium and chromium oxide were increased in the skins with comparing to the used chromium sulfate in the process, and the increasing of chromium sulfate in tanning will cause high levels of hexavalent chromium in the leather layers more than the increase of chromium sulfate in re-tanning.

(Bacardit et al., 2017) studied the effect of temperature, UV radiation, and relative humidity on wet-bright leather aging. It was concluded that relative humidity and temperature are the two parameters that have impacts on wet-bright leather aging. Relative humidity and temperature cause mechanical degradation, because both affect shrinkage temperature, grain distension, and tear load. Temperature causes also organoleptic degradation and it affects chemical degradation.

(Sawalha et al. 2020a) studied the pollution loads from leather tanning industry wastewater in Palestine, wastewater samples from all manufacturing processes were collected, analyzed, and physical characteristics like COD, TS, chromium and pH were compared. It was found that about 10 m^3 of wastewater are generated when processing 1 ton of hide, chemical and physical characteristics of wastewater differ according to the process of manufacture, the total generated pollution loads from leather industry were too high: 29 ton of organic pollutants, 6 ton of total chromium, and 365 of total solids.

(Sawalha et al., 2020b) studied new technologies to treat generated wastewater from tanneries, there were different options for sodium sulfide and chromium substitution and resource recovery, solid wastes composting, and proteins and fats recovery. It was recommended to recycle valuable resources like chromium and sodium sulfide from liquid waste because using new technologies requires a lot of investment and effort, the recovery of materials experiments should be in industrial and pilot-scale not only in lab scale. Economic and environmental improvement requires cleaner production measures, and the most applicable option is resource recovery that does not require a lot of new technologies and cost.

(Sawalha et al., 2019) studied physical and chemical characteristics of generated wastewater from the processing of sheepskins and cowhides. Chemical oxygen demand (COD), total suspended solids (TSS), total dissolved solids (TDS), total solids (TS), chromium, chlorides, and ammonia were measured. The results showed that the highest COD was in liming process, the highest pH was in the tanning process, and the chromium uptake was 46.6 % which is low, and this low uptake indicates that there is a need for cleaner production in local tanneries.

(Al-Jabari et al., 2020) studied the characteristics of wastewater from seven tanneries in Hebron city, all processes in these tanneries were monitored, and cleaner production options were identified and evaluated. It is found that the efficiency of the tanning process is from low to medium, and it is found that the most practical cleaner production option is to improve the operating conditions of the "tanning" process to increase chromium uptake, and this needs an experimental study to know the impacts on leather quality.

Based on the reviewed literature, one of the cleaner production options was to replace chromium tanning with vegetable tanning, Aluminum, Titanium, or Zirconium, but the companies will not accept that, because chromium tanning has the best leathers' quality results. Another option was to recover chromium from the tanning process to use in the post-tanning process, but it is rejected by the companies because this method leaves spots on the leather. Establishing a composting plant to treat free-chromium solid waste is a good solution but it is not accepted because of its cost, also chromium solid waste remains a problem because it cannot be treated. Using the chilling unit to reserve leathers instead of using salts reduces the use of salts and water, but it requires a place and cost for the chilling unit. Establishing the filtration unit to treat lime and chromium effluent to use in the next stages is a good option to reduce water pollution, but it requires a place and cost for the filtration unit too. It was found that the most feasible option technically and economically for Palestinian tanneries is to find a method to increase chromium uptake in leathers. Thus, the chromium tanning method will be tested by changing some variants like: chromium concentration and water temperature. Then, the most appropriate conditions according to chromium exhaustion and leathers' quality will be chosen as a cleaner production practice.

Chapter Four

Materials and Methods

After reviewing the literature and making several visits to the local Palestinian tanneries, two cleaner production options were seen feasible to be applicable in Palestinian tanneries:

1. High-exhaustion tanning by increasing temperature while fixing the water volume and chromium concentration.
2. Variation of chromium concentration in water used in tanning with fixed temperature.

Thus, the selected cleaner production approach was: process modification in tanning process as shown in figure (4.1):

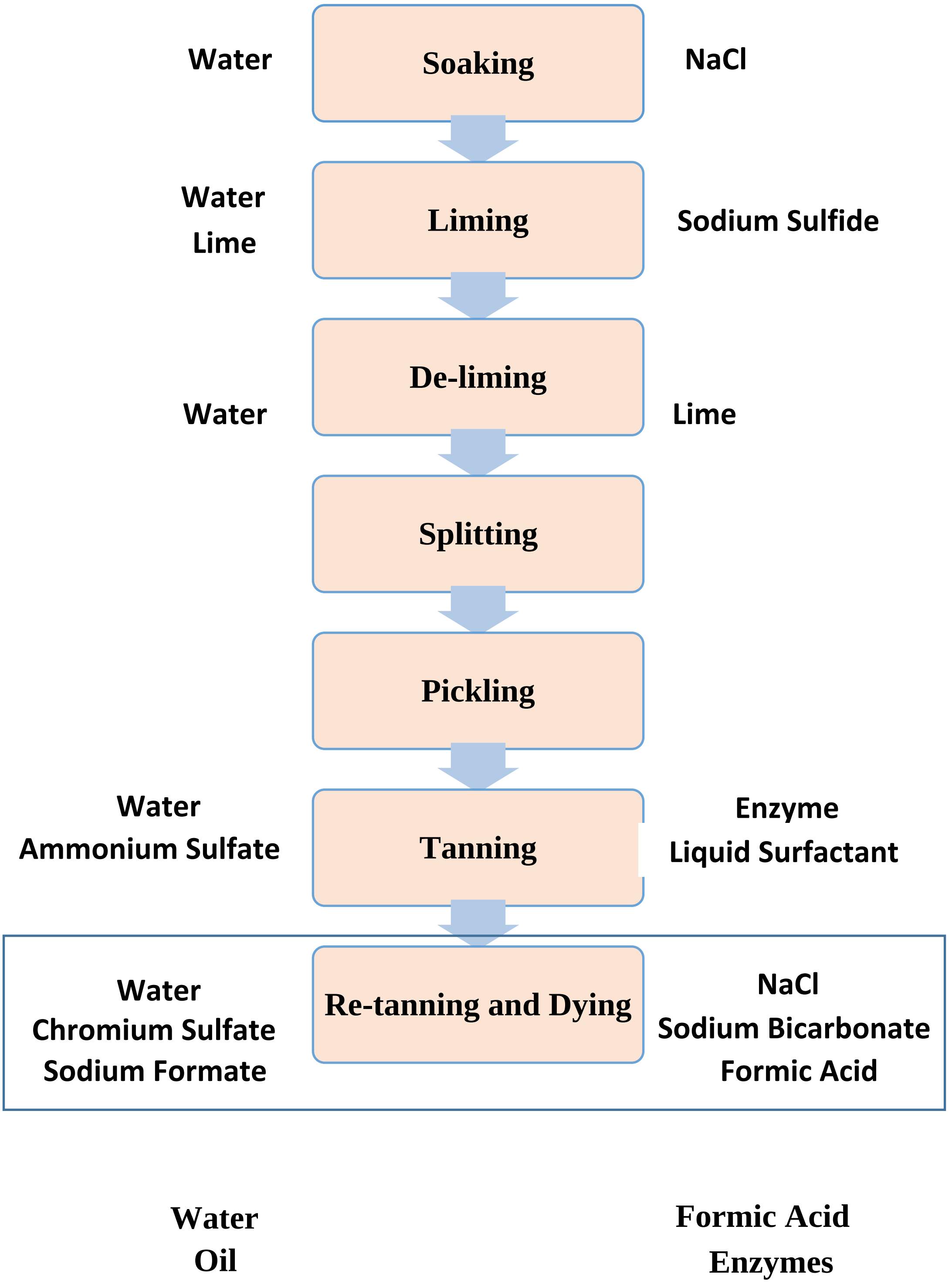

Figure (4.1): Flow Chart for Leather Processing with Selecting the Targeted Process for Cleaner Production Application

And to carry out the required experiments for the selected two cleaner production options, the following materials were brought, and the following methods were carried out:

4.1 Materials:

Table (4.1) shows the materials used, their purities, and their sources.

Table (4.1): Used Materials in Experiments

Material	Purity	Source
Industrial salt	99 % w/w	Dead Sea Salt Company- Palestine
Sodium formate	75 % w/w	Perstorp Specially Chemicals AB-Sweden
Soap	30 % w/w	TFL Ledertechnik GmbH-Germany
Formic acid	80 % w/w	Perstorp Specially Chemicals AB-Sweden
Chromium sulfate	80 % w/w	Völpker Special Products GmbH - Germany
Sodium bicarbonate	80 % w/w	TATA Chemicals Europe-UK
Kestra (Chestnut tree bark to give leather fullness)		India or South Africa
Sestian F and QB (Enzymes that open pores of the leather and allow it to absorb oil and dye)		TFL Ledertechnik GmbH-Germany
Sestian PL (Enzymes that give leather softness)		TFL Ledertechnik GmbH-Germany
NF oil (Oil to give elasticity)		TFL Ledertechnik GmbH-Germany
Dye		Italy, Turkey, China, or India
Sheepskins		Herbawi Tannery in Nablus
Cowhides		Zaatari Tannery in Hebron

4.2 Methods:

A Lab-scale drum was constructed to carry out tanning experiments in the chemical engineering laboratory at An-Najah National University. Then the re-pickling, tanning, re-tanning, and dying processes were carried out for the brought skin/hide with the variation of chromium concentration and water temperature. After that, the chromium concentration was measured in the produced water from tanning, and the tensile strength was measured for the produced leather after dying. These methods will be addressed in detail below:

Lab-scale Drum Construction: A lab-scale drum was constructed by based on specifications in Dose Tannery Machine Brochure (GmbH, 2021). The specifications are shown in Table (4.2):

Table (4.2): Lab-Scale Drum Specifications

Material of Construction	**Drum Diameter**	**Drum Width**	**Drum Volume**	**Drum Speed**	**Motor Power**	**Heating**
Stainless Steel	40 cm	20 cm	25 Litre	5/50 rpm	0.1 kw	1 kw

The constructed lab-scale drum is shown in figure (4.2):

Figure (4.2): Constructed Lab-Scale Drum

Leather Processing: Sheepskins and cowhides were brought after the pickling process from local tanneries. The traditional re-pickling, tanning, re-tanning, and dying processes were carried out using the Nablus tannery procedure for all samples of sheepskins and cowhides as follows (the percentages that will appear here are according to skin/hide weight):

- Re-pickling:

A 20 % w/w salt and 200 % w/w water are added to the drum to rotate for 0.5 hr., then skin/hide sample is added to the drum to rotate for 1 hr., 1 % w/w sodium formate and 3 % w/w soap are added after that to rotate for 1 hr., and finally 2.5 % w/w soap is added to rotate for 1 hr., then the skin/hide is rinsed with water only. pH is checked to be about 4.5.

- Tanning:

A 20 % w/w salt and 200 % w/w water are added with skin/hide sample to the drum to rotate for 0.5 hr., 0.8 % w/w formic acid with 20 % w/w concentration is added to rotate for 1 hr., 5.5 % w/w chromium sulfate is added to rotate for 1 hr., additional 5.5 % w/w chromium sulfate is added to rotate for 1.5 hr., 10 % w/w sodium formate is added to rotate 45 min., and finally 0.8 % w/w of sodium bicarbonate is added with checking pH to rotate for 45 min. pH is checked to be between 3.8 and 4.

- Re-tanning and dying:

A skin/hide sample is put in the drum with 70 % w/w water and 3 % w/w QB at 30 °C to rotate for 0.5 hr., 6 % w/w Kestra, 1.5 % w/w Sestian F, and 2 % w/w Sestian PL are added to rotate for 40 min., 6 % w/w Kestra, 1.5 % w/w Sestian F, and 2 % w/w Sestian PL are added to rotate for 40 min., 5 % w/w NF oil, and water is added at 50 ˚C to dissolve the oil and rotated overnight, the 1 % w/w formic acid is added to rotate for 0.5 hr. after that water is discharged and 100 % w/w new water is added to rotate for 0.5 hr., and finally 0.5 % w/w dye is added to rotate for 1 hr.

Each sample of skin/hide was processed according to the traditional processes used in Nablus tannery, where the following parameters were varied in the tanning process: water volume, chromium concentration, and temperature.

Table (4.3) shows the tanning processes experimental parameters values, water volume percentage is according to skin/hide weight and chromium concentration is according to water volume.

Table (4.3): Parameter Variation through the Tanning Processes Experiments

Experiment No.	Hides' Type	Temperature (˚C)	Water Volume (% w/w)	Cr Concentration (% w/w)
1	Sheep	35	150	6
2	Sheep	35	100	7
3	Sheep	45	200	5.5
4	Sheep	25	200	4.5
5	Sheep	35	200	5.5
6	Sheep	25	200	3.5
7	Sheep	25	200	5.5
8	Sheep	25	100	11
9	Sheep	25	150	7.3
10	Cow	35	200	3.5
11	Cow	35	200	4.5
12	Cow	45	200	4.5
13	Cow	45	150	7.3
14	Cow	35	150	7.3
15	Cow	45	200	3.5
16	Cow	35	100	11
17	Cow	45	100	11

Measurements of Chromium Uptake:

The chromium amount in the produced wastewater from the tanning process was measured using the Flame Atomic Absorption Spectrometer apparatus (iCE 3000 C113500021 v1.30) at the chemistry department lab at An-Najah National University; using Analytical Methods for Atomic Absorption Spectroscopy (Perkin Elmer Corporation, 1996).

The initial chromium concentration was calculated according to equation (1):

$$Cr_{i\ (ppm)} = \frac{amount\ of\ initial\ chromium\ (mg)}{amount\ of\ input\ water\ (L)} \quad \text{...............................(1)}$$

The atomic spectrometer measures the chromium concentration in the ppm unit for the diluted sample. So, the final chromium concentration was calculated as equation (2):

$$Cr_{f\ (ppm)} = \text{dilution factor} \times \text{measured concentration of the diluted sample....(2)}$$

The chromium uptake was calculated using equation (3):

$$Cr_{\ Uptake}\ (\%) = \frac{Cri - Crf}{Cri} \times 100 \quad \text{................................. (3)}$$

<u>Measurements of Skins Tensile Strength:</u> The tensile strength experiments were carried out for the produced leather from sheepskins, the leather produced from cowhides was not measured due to high thickness.. These experiments were carried out in “Leather Industries Laboratory” in Hebron using “Universal Tensile Testing Machine HED05”. The samples of hide were cut using the cutting machine as dog bone shape, then the sample was put in the “Universal Tensile Testing Machine” to measure tensile strength.

Chapter Five

Results and Discussion

5.1 Results of Chromium Uptake

The results of chromium uptake are given in table (5.1):

Table (5.1): Chromium Concentration and Chromium Uptake Results

Hides' Type	Temperature (˚C)	Water Volume (% w/w)	Cr Concentration (% w/w)	Cr Initial (ppm)	Cr Final (ppm)	Cr Uptake (% w/w)
Sheep	35	150	6	60000	11212	81.31
Sheep	35	100	7	70000	8727	87.53
Sheep	45	200	5.5	55000	8175	85.14
Sheep	25	200	4.5	45000	16533	63.26
Sheep	35	200	5.5	55000	21024	61.77
Sheep	25	200	3.5	35000	7494	78.59
Sheep	25	200	5.5	55000	9981	81.85
Sheep	25	100	11	110000	5137	95.33
Sheep	25	150	7.3	73333	7748	89.43
Cow	35	200	3.5	35000	13487	61.47
Cow	35	200	4.5	45000	11565	74.3
Cow	45	200	4.5	45000	12350	72.56
Cow	45	150	7.3	73333	20302	72.32
Cow	35	150	7.3	73333	10047	86.3
Cow	45	200	3.5	35000	12722	63.65
Cow	35	100	11	110000	20727	81.16
Cow	45	100	11	110000	27515	74.99

As shown in table 5.1, the best condition for maximum chromium uptake was at 25 ˚C and 11 % w/w chromium. This condition is similar to that used in local tanneries but with using water volume of 100 % w/w according to skin/hide weight instead of 200 % w/w. This means that chromium uptake by skin/hide is more when chromium is more concentrated in water and when the amount of water is less relative to the skin/hide weight. Figures (5.1) to (5.3) explain the results obtained for chromium uptake:

Figure (5.1) shows the percentage of chromium uptake at different temperatures for sheepskin at 5.5 % w/w chromium concentration in water:

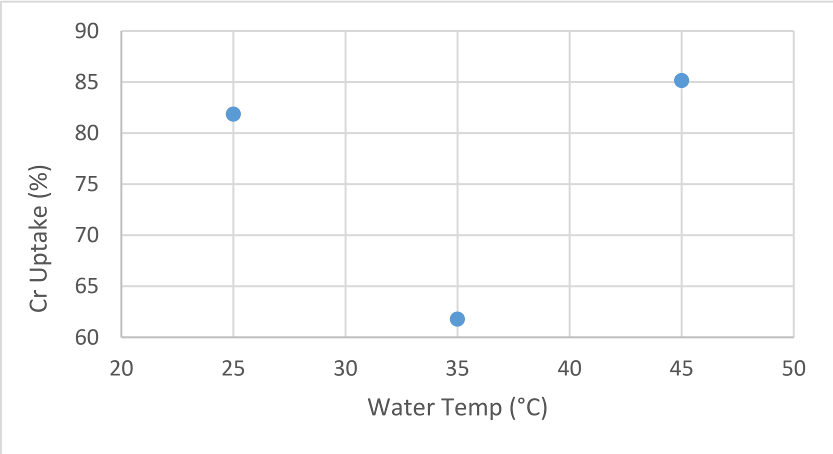

Figure (5.1): The Effect of Temperature on Cr Uptake at 5.5 % w/w Cr for SheepSkin

As shown in figure (5.1), the chromium uptake was decreased by 24.53 % when increasing temperature from 25 to 35 °C, this is because sheepskins are weak in general, and increasing temperature may destroy collagen fibers of skins then the skins will not be able to carry chromium complexes. This result contradicts the result of (Nashy & Eid, 2019), which showed that by increasing temperature from 25 to 35 °C, the chromium uptake was increased (the percentage of increasing was 6.33 %). However, (Nashy & Eid, 2019) used cowhides that withstand high temperatures.

By looking again at figure (5.1), it is observed that by increasing temperature from 25 to 45 °C, the chromium uptake was increased by 4.02 %, because of the increase of water ionization constant which leads to the larger interacting complexes, these larger complexes are more fixed to protein fibers (Nashy & Eid, 2019). This result is similar to the result of (Nashy & Eid, 2019), which showed that by increasing temperature from 25 to 45 °C, the chromium uptake was increased by 7.16 %. On the other hand, when looking at the table (5.1), it is observed that for cowhide; by increasing temperature from 35 to 45 °C (at 4.5 % chromium concentration), the chromium uptake was decreased by 2.34 %, and by increasing temperature from 35 to 45 °C (at 7.3 % chromium concentration), the chromium uptake was decreased by 16.20 %. Moreover, by increasing temperature from 35 to 45 °C (at 7.3 % chromium concentration), the chromium uptake was decreased by 7.60 %, and these results contradict the result of (Nashy & Eid, 2019), which showed that by increasing temperature from 35 to 45 °C, the chromium uptake was slightly increased by 0.78 %.

This means, that the relationship between increasing temperature and chromium uptake is not clear, increasing temperature may destroy the skin/hide collagen fibers then the chromium uptake will be decreased, or it will increase the ionization constant of water to make larger complexes to be more fixed to the skin/hide then the chromium uptake will be increased. So, the increasing temperature is not a promising approach for cleaner production in tanning process; especially when using sheepskins.

Figure (5.2) shows the percentage of chromium uptake at different chromium concentrations in water at 25 °C for sheepskin:

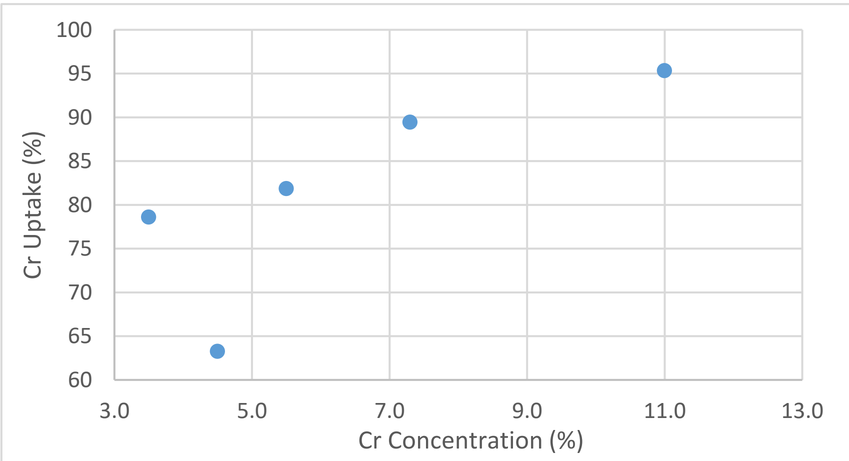

Figure (5.2): The Effect of Cr Concentration on Cr Uptake at 25 °C for SheepSkin

Figure (5.3) shows the percentage of chromium uptake at different chromium concentrations in water at 35 °C for cowhide:

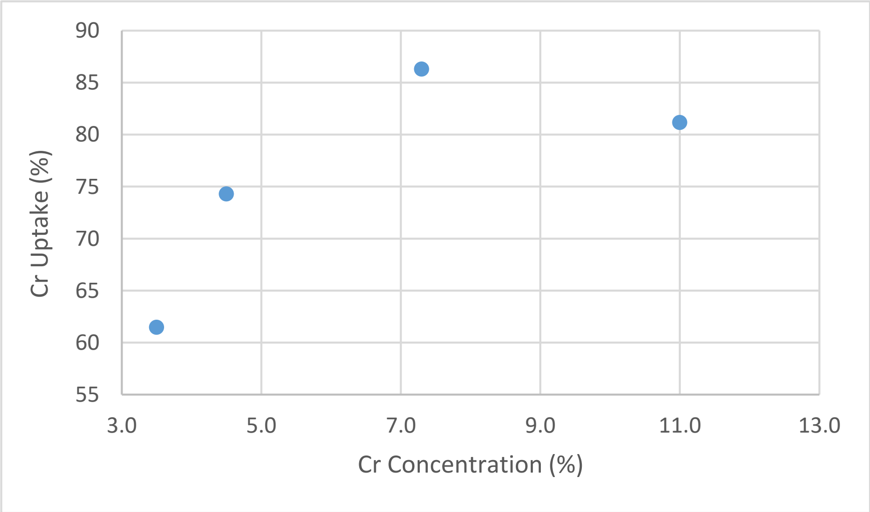

Figure (5.3): The Effect of Cr Concentration on Cr Uptake at 35 °C for CowHide

As shown in figures (5.2) and (5.3), in general, the chromium uptake was increased with increasing chromium concentration in water, because when the chromium concentration increases, the maximum reaction will happen between chromium and collagen structure of the hide, this will make a chemical bonding between the chromium and the hide, and if there is an excess amount of chromium, it will remain as soluble chromium in the hide (Fuck et al., 2011).

When looking at the table (5.1), it is noticed that by increasing chromium concentration from 3.5 to 5.5 % for sheepskin at 25 °C, the chromium uptake by skins was increased by 4.15 %. Moreover, for cowhide when increasing chromium concentration from 3.5 to 4.5 % at 35 °C, the chromium uptake by hides was increased by 20.87 %. These results match (Fuck et al., 2011) findings which showed that when increasing chromium concentration from 6 to 9 %, the chromium content in tanned leather was increased by 3.65 %.

5.2 Results of Tensile Strength

The results of tensile strength for sheepskin were as follows:

Table (5.2): Hides' Tensile Strength Results

Hides' Type	Temperature (˚C)	Water (%)	Cr (%)	Tensile Strength (MPa)
Sheep	35	150	6	15.75
Sheep	35	100	7	15.14
Sheep	45	200	5.5	8.63
Sheep	25	200	4.5	15.39
Sheep	35	200	5.5	7.96
Sheep	25	200	3.5	13.83
Sheep	25	200	5.5	9.96
Sheep	25	100	11	23.25
Sheep	25	150	7.3	18.27

As shown in table (5.2), the best result for hide tensile strength was at 25 ˚C and 5.5 % w/w chromium concentration as the traditional method with decreasing water volume from 200 to 100 % w/w according to hide weight, this matches the result of chromium uptake. This means that the more chromium absorbed, the better hide quality results, because when decreasing water volume, the chromium concentration increases, this leads to transport of more chromium ions into the fiber structure and more chemical reactions will take place between hide protein and chromium, this reaction will result in stabilizing the fiber by cross-linking (Nashy & Eid, 2019). These results match the results of (Nashy & Eid, 2019) which showed that when increasing the chromium concentration in the tanning process, the chromium exhaustion was increased, and the mechanical properties were improved because of cross-linking with fibers of protein.

Figure (5.4) shows the tensile strength of hides at 5.5 % chromium concentration with different temperatures for sheepskin:

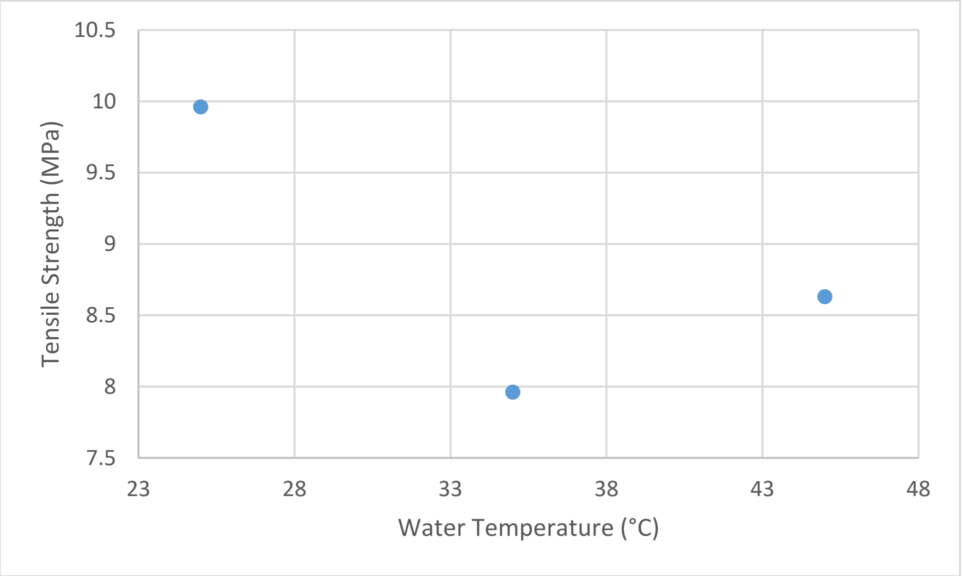

Figure (5.4): Effect of Temperature on Tensile Strength at 5.5 % w/w Cr for SheepSkin

As shown in figure (5.4), the tensile strength is decreased when increasing temperature, because when the temperature is increased, a break down happens in the bonds between collagen and tanning agents because of the radicals reactions, cross-linking quality decreases, then the hide quality decreases (Bacardit et al., 2017). These results match the results of (Bacardit et al., 2017) study which showed that increasing temperature caused mechanical degradation for the leather, and increasing temperature affects the physical properties of grain distension tear and tear load. Moreover, it affects dry rubbing, wet rubbing, organoleptic degradation, and chemical degradation.3

Figure (5.5) shows the tensile strength of hides at a temperature of 25 ˚C with different chromium concentrations for sheepskin:

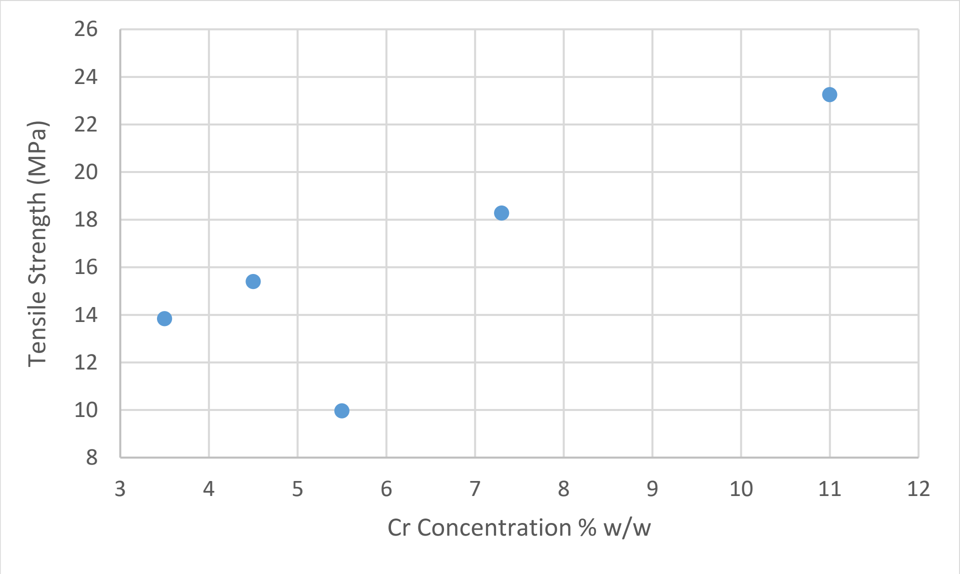

Figure (5.5): Effect of Cr Concentration on Tensile Strength at 25 °C for SheepSkin

As shown in figure (5.5), the tensile strength is increased when chromium concentration is increased, because the oxidation of chromium into hexavalent chromium increases and hexavalent chromium forms in the layers of the hide, this penetration of hexavalent chromium into hide structure increases the reaction between chromium and interactive groups of collagen, which helps in the conversion of collagen into a stable form and make the hide with individual durability (Basaran et al., 2008). These results match the results of (Basaran et al., 2008) study which showed that leather should have a minimum of 2.5 % of chromium oxide to have durable leather with satisfactory hydrothermal stability and acceptable quality levels, and showed that by increasing chromium concentration from 2 to 6 %, the chromium oxide is increased which provides satisfying performance characteristics for the leather. But the study recommended using a chromium concentration of 4 % for a good leather quality with considering hexavalent chromium formation. The concern of hexavalent chromium formation requires measuring hexavalent chromium in the tanned leather to be sure that the amount of hexavalent chromium does not exceed the limitations that harm humans.

As a result, the best practice for chromium uptake was at 25 ˚C and 5.5 % w/w chromium concentration, because chromium is absorbed more when it is more concentrated in water and when the amount of water is small relative to the hides' weight, because of the increase of contact between hides and chromium. The best experiment for hides' tensile strength was also at 25 ˚C and 5.5 % w/w chromium concentration, because more concentrated chromium, results in better hide quality.

Chapter Six

Conclusions and Recommendations

6.1 Conclusions

There are many options for promoting cleaner production in leather processing like using vegetable tanning instead of chromium tanning, using chromium and lime effluent in the next stages without loss of effectiveness after filtration to remove suspended solids, and installation of a chiller unit to preserve hides to use less amount of salts. But in this research study, it was aimed to change some operating conditions in the tanning process to reduce pollution, without completely changing the process or using other materials, to find a technically and economically feasible cleaner production option. Tow main factors were varied: chromium concentration and water temperature. It was found that at 25 °C water temperature (as traditional method), 5.5 % w/w chromium concentration in water, and 100 % w/w water volume according to skin/hide weight (the half of water volume in traditional method) was the best chromium uptake of 95.33 %, this means that chromium uptake is more by skin/hides when it is more concentrated in water and when the amount of water is small relative to the hide weight. So, the generated water will be less polluted, and there is a saving in water consumption to half the amount. Moreover, the best resulting leather tensile strength was at the same conditions, this means that the best leather quality is obtained when chromium uptake by hides is at the max. On the other side, the rise of temperature above 35 °C may affect the hides' quality, especially sheep hides. In addition, using less chromium concentration baths in leather tanning may result in bad leather quality.

6.2 Recommendations:

It is recommended to study the effect of pH variation in tanning process, and to test the effect of temperatures between 25 and 35 ˚C for leather tanning in chromium uptake and leather quality. The most important additional test to be considered is the determination of hexavalent chromium in the tanned leather and comparing it with the standards. In addition, it is recommended to split cow leathers before tanning, unless it will be very tough to be treated or tested. It’s better to apply cleaner production practices on the tannery’s drum that is made from wood not on the metal drum to avoid any chemical reaction between the used chemicals and drum material. Moreover, it is recommended to apply cleaner production at other stages in the leather processing and not just tanning, for example trying cleaner production techniques on the liming process.

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جامعة النجاح الوطنية
كلية الدراسات العليا

الجدوى الفنية لتطبيق ممارسات الإنتاج النظيف في صناعة دباغة الجلود الفلسطينية

اعداد
منية مسعود

اشراف
د. عبد الرحيم ابو صفا
أ.د. عامر الهموز

قدمت هذه الاطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في هندسة المياه والبيئة، في كلية الدراسات العليا، في جامعة النجاح الوطنية، نابلس، فلسطين.

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الجدوى الفنية لتطبيق ممارسات الإنتاج النظيف في صناعة دباغة الجلود الفلسطينية

إعداد
منية مسعود
إشراف
د. عبد الرحيم ابو صفا
أ.د. عامر الهموز

الملخص

الهدف الرئيسي من هذه الرسالة هو التوصية بممارسات الإنتاج الأنظف التي يمكن تطبيقها على المدابغ الفلسطينية ، بعد دراسة واستقصاء طرق الدباغة التقليدية في المصانع المحلية واختبار ممارسات الإنتاج الأنظف لاختيار أكثرها قابلية للتطبيق.

في هذا المشروع البحثي، تم إنشاء برميل دباغة على نطاق معمل لإجراء عملية الدباغة، وتم جلب الجلود من المدابغ المحلية بعد عملية التخليل، وتم تطبيق طريقة الدباغة التقليدية (مثل مدبغة نابلس) على عينات الجلد / الجلد مع تباين عاملين رئيسيين: تركيز الكروم ودرجة حرارة الماء. تم اختيار القيم المثلى بناءً على امتصاص الكروم والجودة الميكانيكية للجلد. في كل تجربة ، تم تحليل حلول الدباغة الأولية والنهائية لتركيز الكروم. تم الحفاظ على درجة الحرارة ثابتة في كل تجربة باستخدام جهاز التحكم في درجة الحرارة والسخان الكهربائي. تم قياس مقاومة الشد للعينات باستخدام آلة الشد القياسية. وجد أن امتصاص الكروم يتقلب مع تغير درجة حرارة العملية. يزيد امتصاص الكروم مع زيادة تركيز محلول الدباغة. من ناحية أخرى ، تزداد جودة الجلد / الاختباء عند زيادة تركيز الكروم في حمام الدباغة ، ولكنها تنخفض مع زيادة درجة الحرارة. تم الحصول على أفضل النتائج لامتصاص الكروم وجودة الجلد / الجلد عند درجة حرارة الماء 25 درجة مئوية ، مع تركيز الكروم بنسبة 5.5٪

وزن / وزن في الماء (كطريقة تقليدية) ، و 100٪ وزن / وزن حجم الماء وفقًا للجلد / وزن الإخفاء (نصف حجم الماء بالطريقة التقليدية). عند هذه النسبة ، كان امتصاص الكروم 95.33٪ والاستهلاك