ADDIS ABABA UNIVERSITY

COLLEGE OF COMPUTATIONAL AND NATURAL SCIENCE

CENTER FOR ENVIRONMENTAL SCIENCES

RECYCLING OF DUSTED SALT FROM RAW HIDES/SKINS FOR PICKLING OPERATION USING SUPERNATANT (WASTE LIQUOR) FROM CHROME RECOVERY UNIT: A CASE OF DIRE TANNERY

MESFIN GUCHE CHEKOLE

A THESIS SUBMITTED TO CENTRE FOR ENVIRONMENTAL SCIENCE IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN ENVIRONMENTAL SCIENCE

JUNE 2018

ADDIS ABABA, ETHIOPIA

ADDIS ABABA UNIVERSITY

Graduate programs

This is to certify that the thesis prepared by Mesfin Guche, entitled: Recycling of dusted salt from raw hides/skins for pickling operation using supernatant (waste liquor) from chrome recovery unit Submitted in partial fulfillment of the requirements for the Degree of Master of Science in Environmental Science

Signed by the Examining Committee:

Examiner: ______________________ Signature _______________ Date: ____________

Examiner: ______________________ Signature _______________ Date: ____________

Advisor: ________________________Signature _______________Date: ____________

Advisor: ________________________Signature _______________Date:_____________

Chair of Center for Environmental Science or Graduate Program Coordinator

ABSTRACT

Recycling of Dusted Salt from raw Hides/Skins for Pickling Operation using Supernatant (waste liquor) from Chrome Recovery Unit: A Case of Dire Tannery

Mesfine Guche
Addis Ababa University, 2018

Since the scope for green processing is limited in Ethiopia, sodium chloride is widely used to preserve raw hides and skins. It contributes to a high volume of total dissolved solids (TDS) in the soak waste liquor. A large amount of the salt sticking to the hide and skin surface can be removed by shaking the hides mechanically or manually.

Among the different desalting methods DODECA wooden frame was found suitable for desalting skins and hides Though the quantity of salt removed varies with the method of desalting, it is generally in the range of 3.6 – 11.8% on the weight of raw stock taken for desalting and the amount of water used for soaking operation reduced in the range of 4.5 – 4.8 % on account of desalting of raw stock.

Though the dusted salt from desalting operations contains many impurities, a fairly clear salt solution can be obtained by dissolving the salt recovered in water, simply screening it and then clarifying it using poly- aluminum chloride. Demonstrations showed that the salt solution so obtained could be safely used in pickling operations.

Desalting of raw stock reduces the chloride level in the composite tannery wastewater by about 41.9%. Practically, it has been seen that chloride in the composite effluent of a tannery processing salted raw hides/skins to semi-finished leather is reduced from 1560 mg/l to 906.4 mg/l on account of desalting of raw stock, collection and proper disposal of the dusted salt. Though desalting may not directly result in considerable financial benefit, indirect benefits include more efficient soaking and reduction in the volume of soak liquor discharged.

ACKNOWLEDGEMENT

I would like express my gratitude to my advisor , Dr. Beteley Tekola (Assistant Professor) and co-adviser Dr Aynalem Abebe for rendering their invaluable supervision, support and guidance for the accomplishment of this work. I would also like to extend my deepest appreciation to my colleagues AAEPA laboratory members for their dedicated assistance without them the work would not complete. In addition, I am also very much grateful with special thanks to Dr Andualem mekonnen for his noble ideas, comments and showing real concern from the start of this work. Final but not least I would like to thank my families who were providing me great motivation to complete this study.

Table of Contents

List of contents **page**

ABSTRACT III

ACKNOWLEDGEMENT IV

TABLE OF CONTENTS v

LIST OF TABLES viii

LIST OF FIGURES ix

LIST OF ACRONYMS x

CHAPTER ONE: INTRODUCTION 1

1.1. RESEARCH BACKGROUND 1

1.2. STATEMENT OF THE PROBLEM 2

1.3. OBJECTIVES 2

1.3.1. General objectives 2

1.3.2. Specific Objectives 3

1.4. SIGNIFICANCE OF THE STUDY 3

CHAPTER TWO: LITERATURE REVIEW 4

2.1. Leather Manufacturing processes 5

2.2. Tannery Waste 10

2.2.1. Liquid and Gaseous Waste 10

2.2.2. Characteristics of Tannery Solid Wastes 14

2.2.3. Impacts on Human Health and the Environment 15

2.3. Solid Waste Management 16

2.3.1. Integrated Waste Management 17

2.4. Cleaner Production (CP) of Relevance to Wastewater Management 18

2.5. Environmental Legal Frame Work 21

2.6. Leather Tannery Wastewater Treatment 22
2.6.1. Best Available Treatment Technologies (BAT) 22
2.6.1.1. Preliminary treatment 23
2.6.1.2. Primary Treatment 25
2.6.1.3. Secondary (Biological) Treatment 27
2.6.1.3.1. Activated Sludge Treatment (AS) 28
2.7. Effect of Chloride 29
2.8. Salts and Total Dissolved Solids 30
2.9. supernatant 30
2.10. Salt Recovery 31
CHAPTER THREE: STUDY DESIGN AND METHODOLOGY 32
3.1. Description of the Study Area 32
3.2. Materials 32
3.2.1. Construction of Dome type DODECA Wooden Frame 32
3.3. Methodology 34
3.3.1. Investigation and identification of types and sources of tannery wastes ... 34
3.3.2. Determination of the amount of salt generated after wet salted sheep skin desalting 34
3.3.3. Assessment on Tannery Waste Management Practices at dire tannery..... 35
3.3.4. Clarification of dusted salt solution 35
3.3.5. Use of dusted salt in pickling 35
3.3.6. The use of supernatant from chrome recovery plant & dusted salt in pickling 36
3.3.7. Characterization of the Major Types of Tannery Wastes 36
CHAPTER FOUR 39

4. RESULTS AND DISCUSSION 39
4.1. Types and Sources of Tannery Wastes 39
4.2. Generation Rate of dusted salt 39
4.2.1. The salt generated after wet salted sheep skins and hides desalting using dome type dodeca wooden frame 41
4.2.2. Estimations of water and chemicals saved from soaking operations after desalting using dome type Dodeca wooden frame from ten pieces of sheep skins and ten pieces of hides 42
4.3. REUSE OF DUSTED (RECOVERED) SALT IN PICKLING 43
4.3.1. Clarification of dusted salt solution 44
4.3.2. Use of dusted salt in pickling 44
4.3.3. The use of supernatant from chrome recovery plant & dusted salt in pickling 45
4.4. Determination of the final discharged waste water 46
5. CONCLUSION AND RECOMMENDATIONS 47
5.1. Conclusion 47
5.2. Recommendations 48
REFERENCES: 49
ANNEXES 57

LIST OF TABLE

Table 1. Nature and quantity of solid wastes produced from processing 1 ton of raw skins/hides………………………………………………………………….. 14

table 2. Pollution loads discharged in effluents from tannery processing units (iue, 1996)………………………………………………………………………… 20

Table 3 national (ethiopian) and world bank tannery effluent discharge limit to surface water.. 22

Table 4. The salt generated by desalting hides using dome type dodeca wooden fram

table 5.the salt generated by desalting skins using dome type dodeca wooden frame.. 41

table 6. Chemicals used and saved from three soaking operations…………… 42

table 7. Effect of desalting on tds emission from soak yard............................. 43

table 8. Characteristics of clarified dusted salt solution...................................... 44

table 9. Characteristics of supernatant liquor from chrome recovery plant......... 45

table 10. Determination of the final discharged wastewater for hides and skins... 46

LIST OF FIGURE

Figure: 1 simplified inflow and out flow of tanning industry ………………………..4

Figure 2. Leather manufacturing process Flow ……………………………………….9

Figure 3.Little Akaki river being used for vegetable irrigation………………………16

Figure 4. Waste Management Hierarchy……………………………………………..18

Figure 5. Complex-mix activated sludge reactor ………………………..………..29

Figure 6. Dome type Dodeca Wooden Frame………………………………………..33

LIST OF ABBREVIATIONS AND ACRONYMS

^{o}Be	degrees Baume
BOD	biological oxygen demand
CFU	colony forming unit
Cl^-	chloride
COD	chemical oxygen demand
CRU	chrome recovery unit
EPA	environmental protection unit
LIDI	leather industry development institute
mg/l	mili gram per liter
SLC	standard methods for leather chemical analysis
TDS	total dissolved solid
TSS	total suspended solid
VOC	volatile organic carbon

Chapter One: Introduction

1.1. Research Background

Currently there are 27 operating industries in Ethiopia 6 of them are found in Addis Ababa, 15 Oromiya, 1 Tigray,5 Amhara region and consume on average 33, 000 skins and 18, 400 hides per day (CLRI, 2010). From the production process the amount of waste water generated is 12,500 m^3 and 150 tones of solid waste (of which 54.5 tones is dusted salt) (CLRI, 2010). Based on laboratory result the wastewater is characterized by high load of pollutants such as chloride, COD, BOD, TDS etc. The amount of chloride which is high and affecting the aquatic life as well as increase soil salinity at present will be reduced when this study is implemented (CLRI, 2010).

Wet salting is one of the most commonly used hide and skin curing practices in the world. Salt is generally cheap and widely available: it has good dehydrating properties. Curing salt is removed during soaking and discharged in waste soak streams. The salt discharged in the soak liquor increases the total dissolved solids content of ground water.

Of late, the negative environmental implications of saline effluent from tanneries have been the object of increased attention, particularly those aspects related to high total dissolved solids (TDS) and chlorides. Tanneries located in rivers may be able to discharge treated effluent with a high TDS content into the sea (UNIDO, 1996).Alternatively, partially treated tannery effluent may be mixed with domestic sewage, low in TDS, for further treatment where feasible. In all other cases, however, the following measures (or a combination thereof) may be considered:

- ❖ Adopting other curing practices that eliminate the use of sodium chloride, without affecting the quality of raw material and creating other serious forms of pollution
- ❖ Removing the curing salt that remains on surface and reusing it

- Recycling the soak liquor to reduce the quantity of soak liquor discharged
- Applying appropriate cost-effective technology to reduce TDS in the effluent

1.2. Statement of the problem

The leather tannery-industry sector has been hugely contributing to the socio-economic development of the nation in terms of foreign currency earning, job creation and tax generation. However, this sector in general is among the most polluting industrial sectors, being very pollution-intensive (World Bank, 2007). The presence of salt at large amount in the discharge waste water of tanneries highly affects the salinity of the fertile soil which intern reduces the agricultural productivity of the land. In addition to the decrease in productivity of the soil, when the discharged waste water enters to the nearby river, the salinity of the river will increase which results in aquatic life disruption and the salt discharged in the soak liquor increases the total dissolved solids content of ground water. Besides, according to the Ministry of Environment and Forest the permissible discharge limit of chloride is 1000 mg/L (CLRI-UNIDO, 1995). But the current situation of all Ethiopian tanneries shows that the concentration of chloride released every day is above the permissible limit. Therefore to alleviate all the above problems associated with the concentration of salt, the chloride load needs to be adjusted as per the discharge limit by recycling the dusted salt.

1.3. Objectives

1.3.1. General objectives

The general objective of this study is to reduce the environmental pollution caused by the high concentration of salt in tannery waste water discharge by employing salt de-dusting technology using and recycling in using supernatant (waste liquor) from chrome recovery unit for pickling operation

1.3.2. Specific Objectives

- To Recover excess salt from the wet salted hide/skin using locally built dome type dodeca wooden frame
- To use supernatant from chrome recovery unit in pickling operation for reusing of de-dusted salt
- To determine the use of fresh salt in pickling, chloride concentration and volume of spent soak liquor from waste water

1.4. Significance of the study

The study has the following significances

- It helps to reduce the amount of fresh common salt required for curing and pickling processes
- It helps to reduce the quantity of soak liquor discharged
- It helps to minimize the pollution load at the source instead of curing the discharged waste

Chapter Two: Literature review

Production of leather from raw hides and skins has been one of the most important industrial processes since ancient times. For centuries, leather was one of few available materials for the production of high durability garments and footwear (Liu et al., 2013). The principal aim of the leather industry, which plays a significant role in today's global economy, is to transform animal hides/skins into physically and chemically stable material by subjecting them to chemical and mechanical sequential processes, and therefore to obtain products for meeting various needs of people. Leather industry has been categorized as one of highly polluting industries and it has adverse impact on environment because of the generation of huge amount of liquid, solid and gaseous wastes (World Bank, 2007). The simplified inflow and out flow of tanning industry is shown in Figure 1. below.

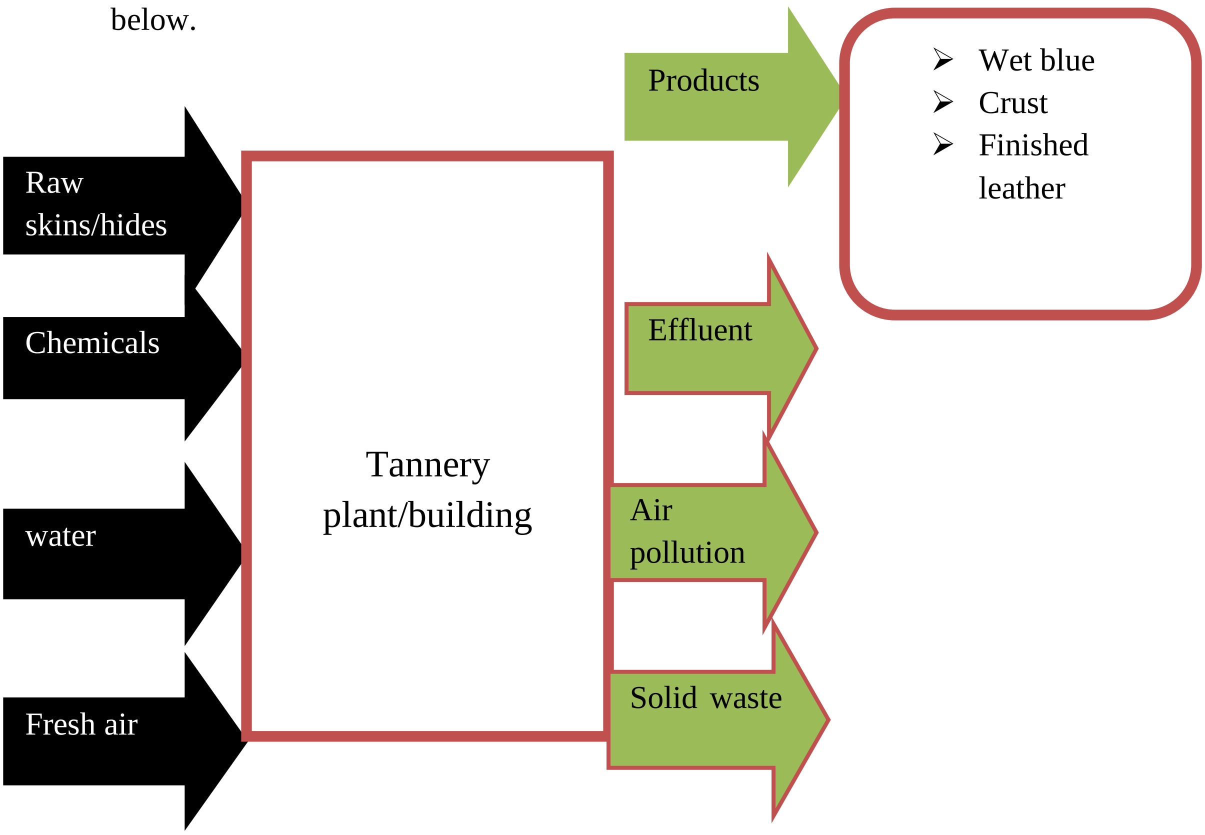

Figure: 1. Simplified inflow and out flow of Tanning Industry

2.1. Leather Manufacturing processes

The leather processing stages can be categorized in to four main stages as follows (Liu et al., 2013).

a) Beam house processes

Generally, the conventional conversion process of hides/skins to leather involves 'do–undo' operations. The conserved skins/hides are first subjected to a trimming process for removing the unwanted parts called skin/hide trimmings, and then they are soaked to restore the lost water due to the common salt applied during curing process and to remove substances like dirt, blood and conservation salt at alkaline condition (pH ranging from 9.5 to 10.5) using wetting agents, sodium carbonate or sodium hydroxide. This is called **soaking** process. After soaking process the skins/hides are subjected to **liming/un-hairing** process which is treating the materials in alkaline (pH ranging from 12 to 13) solution of lime ($Ca(OH)_2$) and sodium sulphide (Na_2S) to remove hair and swell up the skin/hide. After liming/un-hairing process the flesh and fat adhering to the hide/skin is removed by a mechanical process called **fleshing** process. Another mechanical operation called **splitting** after fleshing process is applied most of the time to cattle hides to split into two or three layers or to remove some unwanted layers of the hide. **De-liming** is chemical process performed to decrease the pH to 8.0 to 9.0 so that to remove the lime added during liming process and to make the hide/skin more receptive to the chemicals that will be used in further stages. After de-liming process, hides/skins are exposed to an enzymatic effect for both opening up the structures of hides/skins, and the removal of unwanted proteins by a process called **bating**. Following the bating process, a **degreasing** process is applied for removing the excess natural fat using aqueous emulsification with detergents, or solvent extraction. After degreasing process the hides/skins are treated in a solution composed of salt and acids in acidic solution at an average pH of 2.5 so as to obtain a homogeneous distribution of tanning material that will be applied in the tanning process. This process is called **pickling** process and the product at this stage is named as pickle.

b) Tanning Processes

After the hides/skins are conditioned as above, the tanning process is applied with various tanning materials (materials able to form stable bonds with collagen) in order to provide the leather with a stable form and high thermal stability. Tanning materials such as vegetable Tannins, mineral tanning materials and syntans (synthetic organic tanning materials) are used in tannage. Among mineral tanning materials, chrome tanning is the most widely used in leather production due to the unique features chrome that it gives to the leather; thermal stability. Chrome tanning is carried out in acidic solution at a pH ranging from 2.5 to 3.0 (Liu et al., 2013).

Aluminum and vegetable tanning materials are also widely used in leather production. The product of chrome tanning process is called as wet blue because of its color.

c) Re-Tanning Processes

At re-tanning stage the wet blue hide/skin is changed to crust leather. In this stage, structural differences within wet blue leathers are compensated to obtain uniform structure. It involves the following chemical and mechanical operations.

Shaving – is a mechanical process to even the hide thickness and permit greater precision than is possible by splitting.

Neutralizing – is removal process of the free acid present in the leather, to assure stability in heated conditions and resistant to boiling.

Re-tanning – is a process to give the material the required uniform fullness and ability to retain their consistency after the drying process that tend to flatten the hides and reduce their thickness. This is carried out at a pH ranging from 3.5 to 5.0(Liu et al., 2013).

Fat liquoring – is done to lubricate the dermic fibers to avoid gluing and to provide the finished article with fullness and softness.

Dyeing – is a process of giving the required color characteristics. A good dyeing have good color uniformity, maximum color depth with the least amount of dye possible, good defect cover and high color and light fastness.

Setting out – is a process of pressing the leather to reduce the residual moisture in the hide from 100% to 65-70 % (Liu et al., 2013). It also helps the hide to be widened and the grain to be flattened.

Drying – is an operation to reduce the moisture content from 70% to 20-22% (Liu et al. 2013). It is performed in the company through Vacuum drying, toggle frames, or overhead chain. After this stage, it is called as crust leather and prepared for finishing processes.

d) Finishing Processes

Finishing operation is the mechanical modifications on the appearance of the leather such as elasticity, softness and feels by applying an aesthetic covering polymeric film to the derma.

Finishing operation involves surface coatings and mechanical operations. Some of the finishing processes are given as follows.

Conditioning – is a process to provide moisture in to the dried hide or skin to eliminate the occurrence of cracking for the next operation.

Staking- is mechanical operation applied to increase smoothness of the leather.

Buffing - is a mechanical operation to remove the grain completely and to obtain soft and opaque surface, to make the flesh side of the leather to be refine and smooth, or to remove a more or less significant amount of surface material from low quality hides.

Impregnation – is an operation aims at increasing the ability to adapt to the extension and compression caused by folding, generating a more elegant behavior.

Coating – is the application of natural or synthetic products, generally water-based, for coloring, covering, sealing effects and for giving body to the leather.

Ironing – is pressing operation to make the leather smooth. It is performed in two different machines, flat presses that work in a discontinuous manner or cylindrical rotary presses that work in a continuous manner.

Polishing – is the last finishing operation to provide a shiny appearance and pleasant feel. Figure 2.2 below shows the leather manufacturing process flow. The dashed ellipse in the Figure 2. shows the name of the product output from the corresponding leather processing stages.

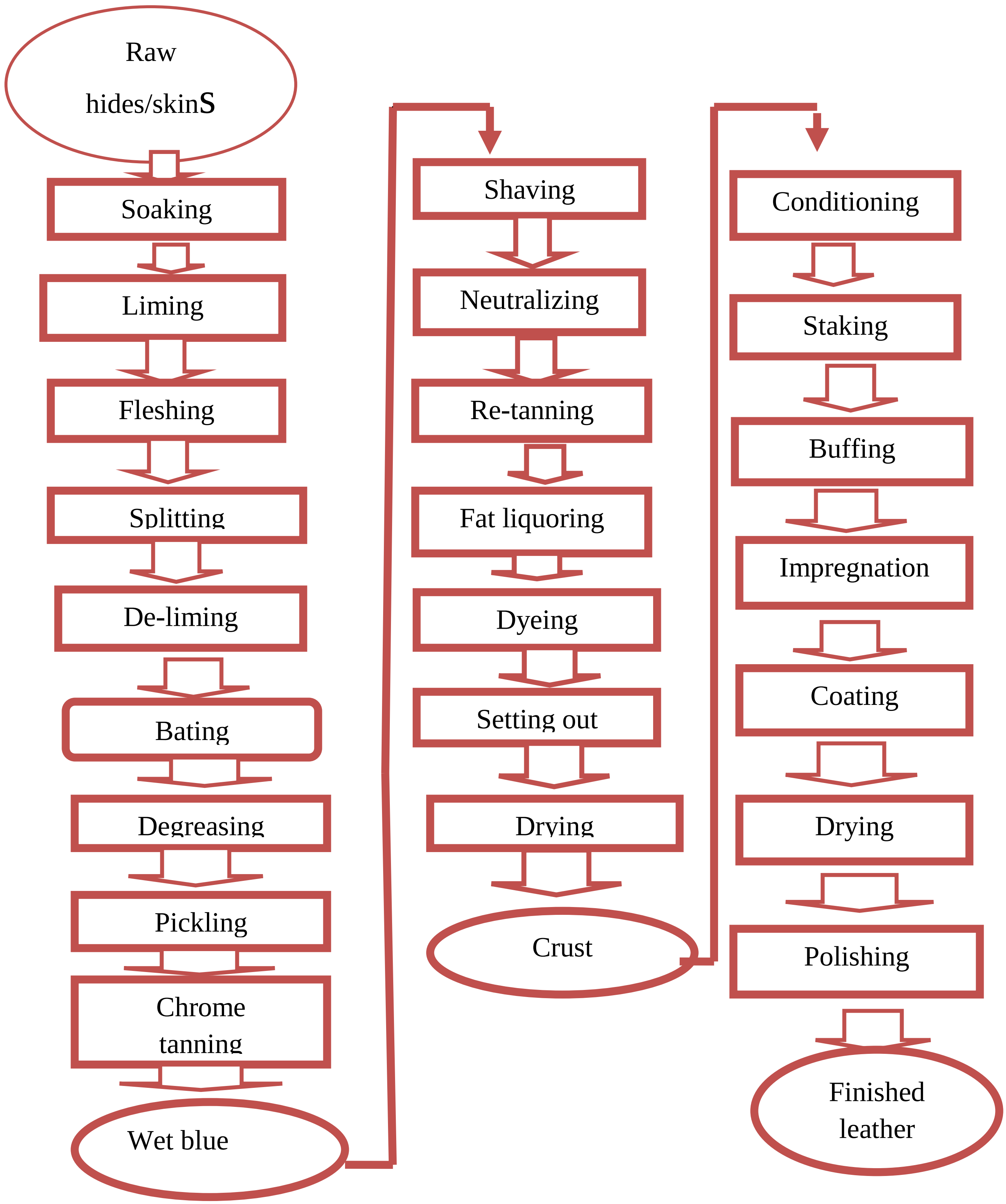

Figure 2. Leather manufacturing process Flow (Liu et al., 2013).

2.2. Tannery Waste

Although the leather industry is environmentally important as a user of the by-product of the meat industry, it is perceived as a consumer of resources and a producer of pollutants that are liquid, solid and gaseous in nature.

2.2.1. Liquid and Gaseous Waste

Tannery effluents are ranked as the highest pollutants among all industrial wastes (Mwinyihija, 2012). The tanning process involves an important consumption of water and generates a complex pollution consisting of a mixture of organic and inorganic substances that rather difficult to treat. A large amount of Chemicals is used to convert raw cattle hides, goat and sheep skins in to leather (Tomaselli, 1999). The chemical reagents consumption is very high. For 1000kg of hides about 400kg of chemicals is needed, including sodium chloride, lime, sodium sulphide, sulphuric acid, basic chromium and others. A considerable part of these chemicals are not absorbed in the production process and is discharged in to the environment. The capacity of world leather process is 15 million tons of hides and skins per year. The waste water discharge from world tanneries is about 600 million m^3 per year. On average 45 -50 m^3 of wastewater is discharged from tanning industry per ton of raw hide processed (World Bank, 2007). The main discharge of waste water originates from wet processing stages in the beam house, the tanning process, and the post-tanning operations. It has been revealed that beam house processes and tanning processes contribute 80–90% of the total pollution load that includes biological oxygen demand (BOD), chemical oxygen demand (COD), total solids (TS), total dissolved solids (TDS), chromium (Cr), sulphides (S^{2-}), sludge, etc. (COTANCE, 2002) . Compared to emissions to water, air emissions occur generally in relatively small quantities. Traditionally tanneries have been associated with odour rather than any other air emissions, although the emissions of organic solvents are a major problem. Whether a tannery has the following air emissions depends on the type of processes employed. Air emissions from tannery are particulate, organic solvents, hydrogen sulphide, ammonia and odor (IPPC, 2000). Emissions to air have effect beyond the tannery site, but also affect the workplace and possibly the health of the tannery workforce. Apart from odours, particular mention should be made here of organic solvent emissions, aerosols and dust (buffing dust and powdery chemicals) (IPPC, 2000).

Particulates

The majority of particulate emissions arise from dry processes, such as milling, buffing and spray finishing operations. These emissions can be abated by using filters, down flow booths, chemical dosing equipment and/or dust free chemicals (dust free bates, liquid dyes and liquid re-tanning agents) (IPPC, 2000).

Organic solvents

The principal source of organic solvent emissions in tanneries is from finishing operations. Abatement techniques, such as scrubber units, are used and are effective in capturing a large part of the organic solvent emissions. Tanneries employing solvent based degreasing processes (mainly sheepskins) have also organic solvent emissions requiring special abatement(IPPC, 2000).

Hydrogen sulphide

The generation of hydrogen sulphide is pH dependent. Hydrogen sulphide can be formed during de-liming and pickling processes and when alkaline effluent streams containing sulphide are mixed with acidic effluent streams. To prevent the generation of hydrogen sulphide, the liquors from the de-liming and pickling processes are treated by means of oxidizing the sulphide with sodium metabisulphite or hydrogen peroxide. This treatment is not applicable for waste lime liquors or mixed effluent due to the presence of too much organic substances. Extraction fans above processing vessels or improved process control can also minimize odors. Optimization of washing processes in order to sufficiently remove sulphide before de-liming and pickling will further reduce the odour emissions. Hydrogen sulphide is also formed in waste water treatment by anaerobic bacteria from sulphates and therefore presents problems in waste water treatment, sludge storage, and dewatering operations. Hydrogen sulphide can also be formed in the sewerage system when sulphide containing effluent is not treated carefully (IPPC, 2000).

Ammonia

Ammonia can be formed in de-liming processes and the dyeing process. Good housekeeping practices, such as effective washing and process control, can minimize these emissions. Extraction fans above processing vessels or improved process control can also minimize odors. These ammonia and hydrogen sulphide emissions can be abated as VOCs, usually by wet scrubbing or bio-filters (IPPC, 2000).

Odour

Odour emissions from raw hides can be controlled by ensuring correct curing procedures, improving storage conditions and ensuring adequate stock rotation. Cool and dry conditions should be maintained in storage facilities and doors should remain closed. Odors may arise from degradation of organic matter or from chemical substances that are also toxic. Odours can arise from storing hides and skins, from beam house operations (sulphides, ammonium), from ammonia releases in dyeing, from VOC released in finishing processes and from the waste water treatment. Odour is one of the main reasons for complaints from neighbors'. Sulphur dioxide emissions might occur during bleaching (IPPC, 2000).

Solid Waste

Apart from liquid and gaseous wastes, large quantities of solid wastes are also generated during leather processing and subsequently during effluent treatment. Although some of the wastes find limited applications, the safe disposal of the bulk of the solid wastes has posed serious problems. Out of which some portion of chromium containing hazardous wastes are also generated. These chrome containing wastes are categorized as hazardous wastes. The main sources of solid wastes are from trimming, fleshing, splitting and shaving processes. A further potential source of solid waste is the sludge from the effluent treatment plant. Tannery effluent treatment plants produce large amounts of sludge: generally, 10% of the total weight of goat and sheep skins and 14% of cow/buffalo hides. The solid waste generation from tannery process in the world is estimated at 6 million tons per year. At an average 80% of solid waste is generated from tanning industry per ton of raw hide processed (Zulfikar,A, 2012). The types of solid wastes generated in a tannery processing one ton of raw skins/hides have been quantified in the table below.

Table 1. Nature and Quantity of Solid Wastes Produced from Processing 1 Ton of Raw Skins/Hides (Zulfikar, 2012).

S.N^o	Nature of solid waste	Quantity (Kg)
1	Salt from handshaking	80
2	Salt from solar pans (not realized)	220
3	Hair (pasting ovine)	100
4	Raw trimmings	40
5	Lime sludge (mostly bovine)	60
6	Fleshing	120
7	Wet blue trimmings (grain splits)	30
8	Chrome splitting (bovine)	65
9	Chrome shaving (mostly bovine)	95
10	Buffing dust (including shaving bovine)	65
11	Dyed trimmings	35
12	Dry sludge from ETP	125

2.2.2. Characteristics of Tannery Solid Wastes

The chemical composition of solid wastes generated from beam house operations (fleshing, trimmings, and splits) depends mainly on a kind and quality of the raw material, treatment type and process conditions. The main components are proteins and fat, up to 10.5% (w/w) for both groups. Water content is high, moisture amounts up to 60%. These wastes contain small amounts of mineral substances, 2-6% (w/w).

Chromium compounds are not present in the material. The tanned leather wastes are mainly useless splits, shavings and trimmings. These waste groups differ mostly in size and shape, the chemical composition is comparable for each. They contain 3-6% (w/w) of fat and about 15% (w/w) of mineral components, including 3.5-4.5% (w/w) of chromium as Cr_2O_3. Sludge from wastewater treatment plants contains mostly water (up to 65% (w/w)), organic substances (30% (w/w)) and chromium (III) compounds (about 2.5% (w/w)) (Zulfikar, 2012). Some research work on tannery sludge shows that the level of chromium content is 500 mg kg^{-1} and this is five folds higher than that should be present in the soil (100 mg kg^{-1}). It has a moisture content (60.6%), pH (7.4), Organic Carbon (20%), Total kjeldhal nitrogen (1.0) and carbon to nitrogen ratio. Due to the low solubility of chromium, only a little (Cr) is bio- available, which means that even when crops are grown in soils treated with sludge relatively high in Cr, phytotoxicity is rarely observed (Zulfikar, 2012).

2.2.3. Impacts on Human Health and the Environment

Untreated or inadequately treated industrial including tannery wastewater poses major threat to the environment and human health among others. In Ethiopia, the impact of water pollution from leather processing industries is already felt. In Addis Ababa, the little and great akaki rivers are highly polluted (Gebre , 2009). Heavy metals such as chromium were found in wastewater-irrigated vegetables such as cabbage, onion and potato in the city (Itanna , 1998) The pollution of little akaki river by pollutants such as BOD and ammonia (NH_3) was also reported by other studies (Melaku et al., 2007). A study conducted in Bahir Dar and Kombolcha industrial sites also claimed that the soil, the irrigation water and the irrigated vegetables were highly polluted, though heavy metal pollution in the irrigation water was not that much, tanneries being among the polluters. The koka bridge site of the upper awash river was also found to have low water quality likely due to factors among which is untreated effluent from factories such as shoa and ethio tanneries. Severe pollution was also reported regarding the Modjo River (polluted by nutrients and other pollutants) by tanneries along the river (Zeleke, 2010). The downward streams of the Sebeta River are also polluted by industries among others (Tassew , 2007). The downstream sites in the river which receive effluent from the Sheba tannery in Tigray region, were also found to have been polluted by hexavalent chromium (Cr^{+6}) exceeding the WHO standard of total chromium in drinking waters (0.005mg/l) as compared with the levels in the upstream points, hexavalent chromium being very toxic to the environment and human health (Gebrekidan , 2009) . Toxic chemicals in tannery effluents pushed communities to lodging serious complaints in the country including in the vicinity of the tannery selected for the actual study.

Figure 3.Little Akaki river being used for vegetable irrigation

2.3. Solid Waste Management

Solid waste management is the collection, transportation, storage, recycling or disposal of solid waste, or the subsequent use of a disposal site that is no longer operational(Federal Negarit Gazeta of FDRE, 2007). It is a complex process because it involves many technologies and disciplines. These include technologies associated with the generation (including source reduction), on-site handling and storage, collection, transfer and transportation, processing, and disposal of solid wastes. All of these processes have to be carried out within existing legal, social, and environmental guidelines that protect the public health and the environment and are aesthetically and economically acceptable. The objective of solid waste management is to reduce the quantity of solid waste disposed off on land by recovery of materials and energy from solid waste (http://en.wikipedia.org/wiki/Waste_hierarch)

2.3.1. Integrated Waste Management

Integrated waste management (IWM) can be defined as the selection and application of suitable techniques, technologies, and management programs to achieve specific waste management objectives and goals (http://en.wikipedia.org/wiki/Waste_hierarch). To be responsive to public attitudes, the disciplines that must be considered in integrated solid waste management include administrative, financial, legal, architectural, planning, environmental, and engineering functions. For a successful integrated solid waste management plan, it is necessary that all these disciplines communicate and interact with each other in a positive interdisciplinary relationship. The four basic waste management options (strategies) for IWM are: (1) source reduction, (2) recycling and composting, (3) combustion (waste-to-energy facilities), and (4) landfills.Figure4. below shows waste management hierarchy(http://en.wikipedia.org/wiki/Waste_hierarch.

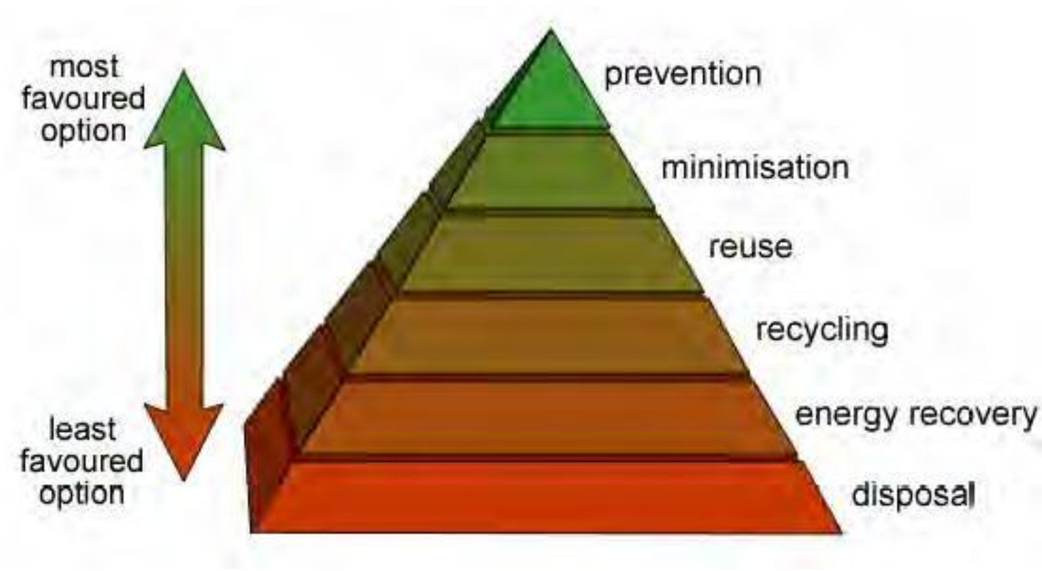

Figure 4. Waste Management Hierarchy

2.4. Cleaner Production (CP) of Relevance to Wastewater Management

CP as pollution prevention approach does play a huge role in reducing the quality (type of pollutants) and quantity of waste water generated in leather processing .Material balance in beam house processing section (per processing one ton of raw hide) indicated that CP practice in that section enabled a pollution reduction from that section of 50%, 50%, 31%, 52%, 52%, 60%, 30% and 100% for parameters of effluent volume, total lime, inorganic solids, COD, BOD, salt, sulfide and NH_3-N respectively (UNEP, 1996). Significant pollutant reduction was also claimed through CP in beam house processing which is the major source of organic matter (approximately 75% of the total load in the waste water) and total suspended solids, the liming/deharing process being the major contributor (World Bank ,2007).Accordingly, hair saving through enzymatic dehairing reduces COD by 40-50%; filtration to recover hair in conventional lime dehairing reduces COD by 15-20% and total nitrogen by 25-30% in mixed tannery effluent; and lime float recycling reduces COD by 30-40%, nitrogen by up to 35%, sulphide use by up to 40% and lime use up to 50%. Around 60% of total chloride in the tannery effluent is due to the curing process using salt, which is released in the soaking effluent, the rest contributed by pickling and a few by the tanning and dyeing operations. Then, CP in this case to reduce chlorides in the effluent involves natural drying of skins; chilling/ice preservation for short term storage; antiseptics usage for long-term storage; trimming before curing and other operations; mechanical/manual removal of salt to save it before soaking; salt free pickling; ammonium free deliming (using week ac ids or easters); CO_2 deliming instead of using ammonium salts; short floats in tanning to reduce chemical; direct recycling of pickling float; direct recycling of tanning floats and recycling of chrome recovery plant supernatant. In relation to sulphide reduction from the deliming/hairing waste stream through CP, actions such as enzymatic deharing (rather than using inorganic sulfide), keeping sulfide-lime overall solution percent of 20-50 for a conventional lime dehairing process and keeping sulfide-containing liquor at alkaline P^H (P^H >10) are recommended. Ammonia salts used in the tanning process are the major contributors (up to 40%) of ammonia nitrogen in tannery effluents, others sources being dyeing and animal proteins in beam house operations. On the other hand, total kjeldhal nitrogen (TKN) is mainly contributed up to 85% by liming in the beam house operations. Accordingly, use of ammonium-free deliming such as week acids and CP measures used to reduce organic load may also be considered to reduce nitrogen load in tannery waste waters. The detailed role of CP in reducing pollutants of effluent was also reported (table 2). In Ethiopia, CP practices are found to be inexistent or inadequately existent in many tanneries. A study on CP for solid waste management in Addis Ababa tannery (AAT) reported that CP practices such as proper weighing of chemicals, green fleshing and lime splitting were absent in the tannery (Belay W.and Andulem A., 2008). The study claimed that those CP options, if implemented, could have significantly reduced process chemical usage and production cost along with prevention of environmental pollution. The recommended CP options do also have a decisive role in reducing the amount of chemical pollutants in waste water obviously easing the burden on waste water treatment plants. Another study on waste water management in Batu tannery, Ethiopia also reported the inexistence of CP practices creating further burden on the waste water treatment plant that was physically observed to be inefficient.

Table 2. Pollution loads discharged in effluents from tannery processing units (IUE, 1996)

Process	Tech	**Pollution load (Kg/ton of raw hide); WW (m^3)**							
		WW	**SS**	**COD**	**BOD_5**	**Cr**	**S^{2-}**	**NH_3-N**	**Cl^-**
soaking	**C**	7-9	11-17	22-33	7-11	-	-	0.1-0.2	85-113
	A	2.0	11-17	20-25	7-9	-	-	0.1-0.2	5-10
Liming	**C**	9-15	53-97	79-122	28-45	-	3.9-8.7	0.4-0.5	5-15
	A	4.5	14-26	46-65	16-24	-	0.4-0.7	0.1-0.2	1-2
Tanning	**C**	3-5	5-10	7-11	2-4	2-5	-	0.6-0.9	40-60
	A	0.5	1-2	7-11	2-4	0.05-0.1	-	0.1-0.2	20-35
Finishing	**C**	1-3	0-2	0.5	0-2	-	-	-	-
	A	0	0-2	0	0	-	-	-	-
Total	**C**	36-56	83-149	145-231	50-86	3-7	4-9	4.6	137-202
	A	12	35-61	96-133	33-51	0.15-0.5	0.4-0.8	0.6-1.2	30-55
Technology; C: Conventional; A: Advanced/Cleaner production; WW: Wastewater									

2.5. Environmental Legal Frame Work

One of the mechanisms to control water pollution is law promulgation and enforcement. In Ethiopia, citizens' right to a clean, healthy environment and to sustainable development are the two environmental objectives in the national constitutions Article 44 (1), Article 43(1). Among the specific objectives of the national environmental policy are sustainable use of non-renewable natural resources and cost effective prevention of pollution with its guiding principles such as pollution prevention and minimization, enforceable pollution standard setting and monitoring, polluter-pays approach and clear linkage between pollution control and other sector policies (CSE, 1997). In addition, the industrial sector pollution control policy has the objective of limiting the release of industrial (including tannery) hazardous and other pollutants to the environment. The country's environmental pollution control proclamation imposes a legal duty that no person shall pollute the environment, incentive mechanism such as exemption of custom duty for import of pollution control equipment being part of it (article 10 (1,2)) (FEPA, 2003). The country also has environmental impact assessment (EIA) law with an incentive mechanism such as financial and technical support by regulators namely regional and federal EPAs (article 16 (1, 2) (FEPA, 2003). Standards were set as national level to regulate effluent release from tanneries (Table 3.).

Table 3 National (Ethiopian) and World Bank tannery effluent discharge limit to surface water

Parameter	**Unit**	**National**	**World Bank**
Temperature	^{0}C	40	
PH	PH units	6-9	6-9
BOD5	mg/l	200 (or 90% removal)	50
COD	mg/l	500	250
SS	mg/l	50	50
Total ammonia (as N)	mg/l	30	10
Total nitrogen(As N)	mg/l	60 (or 80% removal)	10
Total phosphorous(as P)	mg/l	10 (or 80% removal)	2
Total chromium	mg/l	2	0.5
Sulphide (as S^{2}-)	mg/l	1	1

2.6. Leather Tannery Wastewater Treatment

2.6.1. Best Available Treatment Technologies (BAT)

Protection of water bodies from harmful pollutants is the main objective of wastewater treatment (UNIDO, 2011). Hence the appropriate wastewater treatment technology must be carefully selected considering multiple objectives such as technical, economical, legal and environmental aspects to increase the chance of success of the selected alternative (WHO, 1997). There are a number of available in-use treatment technologies for tannery effluents in the world. However, BAT for a particular industry depends on factors such as land availability, local climate and available resources among others. Although there are

BATs in the world, contextualized and adapted use of the technologies for a particular industry is important. Consequently, there are several criteria based on which to select a particular technology among the major ones being efficiency, reliability, land requirement, cost, simplicity, flexibility and sustainability (Von Sperling, 1996).

2.6.1.1. Preliminary treatment

The role of primary treatment in tanneries is to remove large particles such as sand, grit and grease apart from highly reducing the concentrations of chrome and sulfides before the effluent joins the main treatment plant. Accordingly, BAT in pretreatment of tannery effluents includes coarse and fine screens, equalization tanks, sulfide oxidation system-sometimes performed in equalization tanks, chrome recovery system and floating object removing system apart from segregation of streams namely lime stream, chrome stream, soaking stream, post-tanning stream and the rest stream so as to facilitate efficient separate treatments and valuable resource recovery (UNIDO, 2011) .consequently, some of the cp techniques that reduce pollutants in the general effluent to the conventional wastewater treatment plant may also be considered as vital effluent pretreatment processes as they lessen the burden on the conventional treatment plant.

Chrome recovery involves precipitating the spent tanning liquor (after sieving to remove particles and fiber) as chrome hydroxide sludge by treating it with a base such as hydroxide of sodium or magnesium followed by addition of concentrated sulfuric acid to dissolve the sludge to change it to chromium salt solution of Cr (OH) SO_4 which is used for tanning (UNIDO, 2011). This recovery mechanism can enable 95-98% chrome recovery with very attractive economical implications, with the money saved fully or partially covering the operating costs of treatment plants (WHO and UNEP, 1997). Sulfide catalytic oxidation (in a separate or in equalization tanks) usually using $MnSO_4.H_2O$ significantly reduces the concentration of sulfide in the liming/dehairing segregated effluent. This technique is the most economical and widely used BAT of sulfide removal in tannery effluents (LINT, 2009).

Equalization tanks are used to homogenize hydraulic and organic loadings to ensure the desired effluent quality of individual units and the overall treatment system (UNIDO 2011). They solve operational problems, enhance overall treatment efficiency, reduce the size and cost of subsequent treatment processes, improve chemical feed control, reduce process variability and improve efficiency of overloaded treatment plants though they have disadvantages such as big land requirement, odor and additional costs. Screening operations protect further treatment process equipments and enhance process efficiency and reliability, being classified in to course (mesh size: 6-150mm), fine (mesh size < 6mm) and micro (mesh size much less than 6mm). The coarse screens protect pumps, valves and pipelines from damage and clogging while fine screens are used for preliminary and primary treatment. Mechanically cleaned screens are generally preferable due to enhanced process efficiency, and reduced operational and maintenance frequency and costs. Both coarse and fine screens are highly recommended for leather tannery effluent preliminary treatment, the fine screen having the ability of further reducing fine suspended solids in the effluent (UNIDO, 2011). Grit chambers remove large particles such as grit, sand etc that could cause problems such as abrasive wear in mechanical equipment and pipe clogging among others (Metcalf and Eddy, 2003). At least simple non-aerated grit chamber is recommended.

2.6.1.2. Primary Treatment

This stage is designed to remove organic and inorganic solids by the action of gravity (sedimentation) or dissolved air under pressure (dissolved air floatation). Floating materials are also removed at this stage through skimming operation. Removal of around 25-50% of BOD_5, 50-70% of TSS and 65% of the oil and grease can be achieved during primary treatment. Circular and rectangular tanks are used with continuous scum and sludge removal (UNIDO, 2007).

Circular clarifiers are better in terms of sludge removal mechanism, maintenance requirement/cost and in-tank thickening while the rectangular ones are better regarding space requirement, capital cost, allowing of separate flow splitting structures and sludge pumping stations , However, circular clarifiers and recommended for tannery wastewater treatment(UNIDO, 2007)

Chemically enhanced primary treatment is mostly used in wastewater treatment to enhance pollutant removal efficiency of TSS, BOD, heavy metals and nutrients (especially phosphorous) apart from allowing increased solids and hydraulic loading rates. It involves salt (iron and aluminum salts) and/or lime addition for coagulation (destabilization) of particles and polyelectrolyte addition for flocculation (aggregation) of particles, the most common chemicals for this purpose being alum ($Al_2(SO_4)_3.18H_2O$) or $Al_2(SO_4)_3.14H_2O$), ferric chloride ($FeCl_3$), calcium hydroxide ($Ca(OH)_2$), aluminum chloride ($AlCl_3$) and ferrous sulfate or copperas ($FeSO_4.7H_2O$). Chemical precipitation for phosphorous and heavy metal removal is also achieved with coagulation and flocculation processes by the addition of multivalent ions (Ca^{2+}, Fe^{3+}, Al^{3+}), polymers being effectively used along with alum and lime as flocculation aids. For instance, addition of lime results in reaction with natural bicarbonate alkalinity to precipitate calcium carbonate. But at pH > 10, excess calcium ions react with the phosphate to precipitate it as calcium hydroxyl apatite ($Ca_{10}(PO_4)_6(OH)_2$). Similarity, addition of trivalent iron and aluminum ions results in precipitation in the form of aluminum and iron phosphates (Metcalf and Eddy, 2003). Although the chemical enhancement of the primary treatment incuse additional cost, it may be compensated by the reduction in cost from the operation of secondary treatment as the burden on it is significantly reduced. It may also be justified by the discharge standard compliance requirements that may incur even much more cost to the industry in question if not achieved.

High rate clarifiers such as inclined plate and tube/lamella/ settlers and dissolved air floatation (DAF) systems permit higher loading rates and enhanced pollutant removal efficiency. Lamella settling is based on the principle of reduced-depth sedimentation (increased surface-area-based settling) where particles are only required to settle to the surface of the tube or plate below. These high rate settlers in primary sedimentation processes are very useful as they are associated with major advantages such as allowing high loading rates, reduced space requirement, rapid start-up times of the system and high effluent quality.

DAF is a mechanism involving the bubbling of air into flocculated wastewater to force flocculated particles to the surface where they will be skimmed (Metcalf and Eddy, 2003). Accordingly, the waste water per-saturated with air will be exposed to a reduction in pressure, which will then be forced through valves or special orifices so that clouds of bubbles are formed downstream of the constriction (Tassew, 2007). Chemically enhanced

DAF system as a primary wastewater treatment can ensure removal efficiency of 70-80% , sometimes up to 90% COD, the floating sludge having 8-10% of solids content that is more cost effective to handle compared to the handling of the only 2-3% solid content sludge achieved by settlement processes (LINT, 2009). DAF has long been used for sludge thickening and removal of ions, organic solids, dissolved oils volatile organic compounds, and algae, being most commonly used for the treatment of industrial effluents. It has advantages such as small tank size requirement, allowing high and variable solids loading rate, high float concentration, removal of low-density particles, short detention times and less space requirement. However, they are associated with high capital and operating cost such as energy cost associated with the aeration process.

2.6.1.3. Secondary (Biological) Treatment

Biological treatment is the next step in the treatment of industrial wastewater, both aerobic and anaerobic biological systems being used with different efficiencies across the world (Durai G., 2011). The aerobic system is better than the anaerobic system in that it has excellent effluent quality, low temperature sensitivity or no heat input and less sensitivity to toxic compounds in the wastewater such as chlorinated compounds. It has also associated with low alkalinity requirement, high nutrient removal, less odor production and short start-up time of usually 2-4 weeks unlike the 2-4 months of the anaerobic processes (Chan, *et al*., 2009). On the other hand, the anaerobic systems are associated with (and hence better than the aerobic systems) low sludge production, low nutrient and oxygen requirement, low energy input and better resource (e.g. energy) recovery.

Both aerobic and anaerobic processes are used in treating tannery wastewater, the widely used technologies being activated sludge (AS) and up flow anaerobic sludge blanket (UASB). Constructed wetlands (CWs) and pond systems (waste stabilization ponds especially aerated facultative ponds) (UNIDO, 2011).are also used for tannery wastewater treatment in some cases, though these treatment approaches are not as well established as conventional treatment systems such as the AS. The AS will be focused in this paper as it is the secondary treatment technology used in the actual industry.

2.6.1.3.1. Activated Sludge Treatment (AS)

AS is the most widely used secondary (biological) treatment system for tannery wastewater (Figure 2.2). It could be the conventional one or its modifications, the most widely used being the complete-mix extended aeration system. The major operational parameters of the process are total influent volume, aeration tank volume, organic loading rate (OLR), mixed liquor suspended solids (MLSS), food to microorganism ratio (F/M) and hydraulic retention time (HRT), other important operational parameters being sludge age (usually not less than 20 days) and return activated sludge (RAS), which is the volume of recycled sludge to the total influent volume (Q) (80-100% in extended aeration process). In addition, the parameters to be regularly monitored are DO I the aeration tan, PH (effective range is 6-9, the optimum being 7.0-7.5), temperature (recommended: 10-30^{o}C), nutrients and sludge volume index (SVI), which is the volume occupied by 1g of activated sludge after setting the aerated mixed liquor in a 1,000ml graduated cylinder for 30 minutes. SVI shows whether the sludge is compact, which is important to control the process and determine pumping requirements of return sludge, well settled sludge having SVI less than hundred. Do must be at least 2mg/l in the aeration tank, the BOD-nitrogen-phosphorus ratio (BOD: N: P) being 100:5:1. Dissolved oxygen above 2mg/l improves nitrification while above 4mg/l increases aeration cost without improving anything (Metcalf and Eddy, 2003).

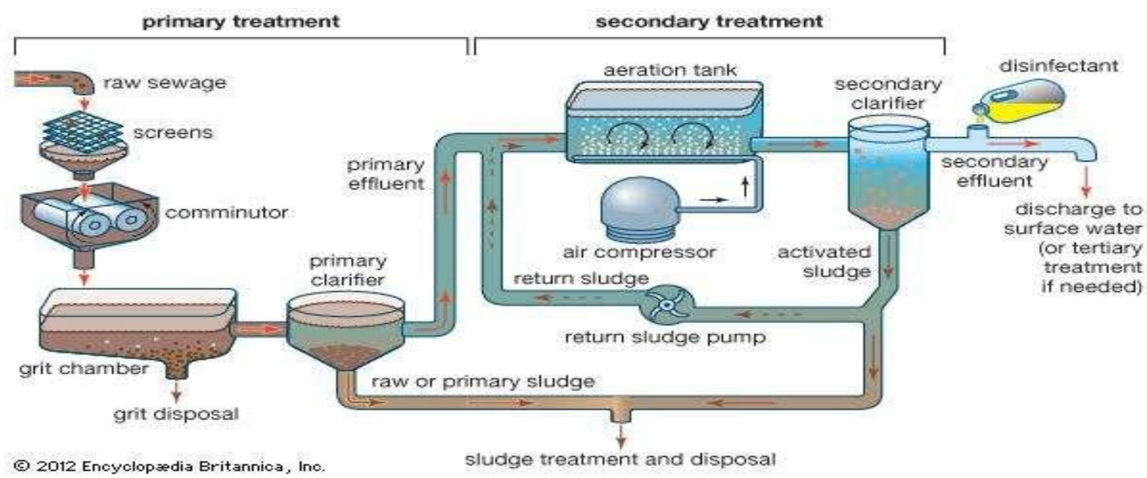

Figure 5. Complex-mix activated sludge reactor (Metcalf and Eddy, 2003)

2.7. Effect of Chloride

The high chloride content in the effluent (1693.7 ± 757.4 mg L-1) can affect aquatic plants and certain species of animals. Each species adapted to low salinities have a certain range of salinities with in which they can survive. However, animals not affected by salinity may be indirectly affected by habitat modification and altered food supply. Aquatic invertebrates, macrophages and plants are generally affected (e.g. in plants, a reduction in growth rates, leaf production and die-back of the growth tips is observed) at salinities over 1000 mg L-1, while more than 4000 mg L-1 affects the survival of some common macrophytes. Related studies have shown that 9 g L-1 of chloride could represent a considerable problem for biological plants . Moreover the impact of curing effluent on terrestrial ecosystems was found as a cause to aridity on impacted soil .

2.8. Salts and Total Dissolved Solids

Salting and other tannery processes contribute to the presence of salts / electrolytes in wastewater streams, measured as Total Dissolved Solids (TDS). Approximately 60 percent of total chloride is produced from salt used for curing, which is subsequently released in the soaking effluent (Munz, 2006). The rest is generated mainly from pickling and, to a lesser extent, tanning and dyeing processes. Additional contributors to TDS include the use of ammonium chloride and sodium sulfate. The TDS concentrations may reach 15,000 mg/l in tannery effluents (LIDI, 2012). Disposal of waste-neutral electrolyte is a significant challenge for leather manufacturing, particularly for those facilities located in land-locked areas. Measures to reduce TDS loads from raw material preservation and processing include the following:

- Use of natural drying of small skins at facilities in suitable warm, dry climates;
- Use of chilling for short-term preservation of freshly processed hides or skins, and / or use of antiseptics to increase storage time;
- Undertake trimming and, where possible, pre-fleshing before curing or other pre-tanning operations;
- Use of mechanical or manual removal of salt from hides and skins before soaking;
- Use of ammonium-free deliming agents (e.g. weak acids or esters) or CO_2 deliming instead of ammonium salts.

2.9. supernatant

A supernatant liquid occurs in the chemical process of precipitation, and it is typically a clear liquid free of precipitate located above the solid during settling. A supernatant is considered a deposit, and the term itself is from the Latin word "supernatant," meaning to float from. The precipitation process is used for the treatment of effluents from the chromium-tanning process including washing floats and liquid from samming. It is based on the recovery of chromium from the effluents and its recycling in to the production process. From the chemical point of view, chromium(III) recovery is a simple process with excellent environmental results, but it needs careful analytical control and it requires special equipments such as a separate tank for collecting spent chrome tanning liquors, material to analyze the chromium content, acidity and alkalinity, a tank with stirrer and PH control for adding the right amount of alkali for the precipitation, a sedimentation tank for chromium hydroxide setting, a filter press or centrifuge for the chromium hydroxide sludge, a tank with stirrer and heating equipment for the re-solution of the chromium hydroxide by concentrated sulphuric acid .

2.10. Salt Recovery

UNIDO through its regional program for pollution control in the tanning industries has been actively looking for solutions to tackle saline tannery effluent. Currently the following technologies are implemented in pilot demonstrations unit (1) mechanical/manual removal of excess salt from wet salted hides and skins (2) reverse osmosis of treated tannery effluent (3) improved solar evaporation (4) recycling of floats in beam house after filtration (5) use of ultra filtration in tannery effluent (Malden, 1997).

Chapter Three: Study Design and Methodology

3.1. Description of the Study Area

Dire tannery is located in the north-western part of Addis Ababa, the capital city of Ethiopia at 9.0626^{O}N, 38.7124^{O}E. Dire Tannery, part of the larger Ethiopian company, Dire tannery industries, processes 600 cattle hides and 5,000 sheep skins per day, with a weekly output of around 80,000 square feet of bovine leather used for shoe uppers and 150,000 square feet of sheep skins used for shoe uppers and lining gloves and garment leathers.

3.2. Materials

Hides and skins were used to produce finished leather for garment, glove and shoe upper. Leather processing chemicals, tannery machineries for processing the raw hides/skins and laboratory equipments (Atomic absorption Spectrophotometer, Oven, digital balance, solid waste sample collection containers (plastic), pH meter, pipette, shaker, wide-necked polyethylene flask, calorimeter, Distillation unit, volumetric flasks) for the characterization of the sample solid wastes were also used.

3.2.1. Construction of Dome type DODECA Wooden Frame

A simple wooden frame of a size (1mx1mx1m) made from local wood was designed and desalting was done by holding the hides at the edges and beating them three times on the frame , the salt was collected manually from the floor. For large hides, four workmen were sufficient and for smaller hides and skins, two workmen were sufficient. The figure below shows the dome type Dodeca wooden frame

Figure 6. Dome type Dodeca Wooden Frame

3.3. Methodology

3.3.1. Investigation and identification of types and sources of tannery wastes

The sources and types of tannery waste generated during manufacturing of different types of finished leather were identified by physical observations and interviewing the foreman working on each stages of leather processing at dire tannery. The observations were made at two units of the tannery (hides and skins unit). The first observation was made at the hides unit in which finished leather for shoe upper is produced and then at skins unit where finished leather for glove and garment are manufactured.

3.3.2. Determination of the amount of salt generated after wet salted sheep skin desalting

To determine the generation rate of each types of desalted salt generated from the tannery, the following methods were used.

- Based on random sampling techniques, samples of ten pieces of wet salted cattle hides being processed to produce finished leather were taken piece by piece from beam house process which are expected to generate the dedusted salt and material balance analysis techniques were applied (i.e. weighing the samples before and after the operations) to determine the generation rate of the dedusted salt.

- In a similar manner, samples of ten pieces of wet salted sheep skins being processed to produce finished leather for glove and garment were randomly taken piece by piece for the operations of leather manufacturing processes which are expected to generate solid waste (i.e. desalting) and material balance analysis techniques were applied to determine the generation rate of the dedusted salt.

3.3.3. Performance of dome type dodeca wooden frame

% performance = (x-y)/(x) x 100

Where x= mass of wet salted hide/skin before desalting

Y= mass of wet salted hide/skin after desalting

3.3.3. Assessment on Tannery Waste Management Practices at dire tannery

In a similar manner, prior to sample collection for the analysis, a visit was made within the compound of dire tannery to observe and assess the existing waste management practices of the tannery. In addition to physical observation, interviews were made with the concerned personnel of the tannery to gather information on how the wastes generated from the tannery are being managed.

3.3.4. Clarification of dusted salt solution

The dusted salt is prepared as a 12% solution. The solution is screened to remove hair, tissue, sand and other insoluble matters and the filtrate is treated with poly aluminum chloride (300 mg/l) and poly-electrolyte (2 mg/l) and allowed to settle for 4 to 6 hours (UNIDO, 2001).

3.3.5. Use of dusted salt in pickling

10 cowhides were taken and cut along the backbone to obtain 2 sides. The left sides were processed by replacing 50% of salt used in pickling with dusted salt. The right sides were

processed with fresh common salt. These trials were done in full-scale production by making marks of identification on the material taken for study. After tanning the sides were assessed and the grain was examined using a microscope.

3.3.6. The use of supernatant from chrome recovery plant & dusted salt in pickling

Recovery of chrome from spent chrome liquor by the process of precipitation were taken With a view to reduce use of fresh salt in pickling and conserving water, the supernatant from chrome recovery plants, which is waste liquor, was used for dissolving dusted salt obtained from desalting.

3.3.7. Characterization of the Major Types of Tannery Wastes

In order to determine selected physicochemical parameters (pH, TDS, chloride, sulphate, TSS, proteolytic bacterial count and chromium content) of the liquid wastes generated during leather manufacturing processes at dire tannery, the following methods were used.

Determination of pH

The P^H of the sample liquid wastes was determined by shaking five gram of sample wastes in 100ml of distilled water for 16 – 24 hours followed by direct measurement of the pH according to the standard methods of SLC.

Determination of TDS

The TDS of the sample liquid wastes were determined by taking a known quantity of liquid sample in a crucible of known weight and the sample is filtered through what man paper no.44 and the unfiltrable solids remain on the filter paper while dissolved solids go in solution through the filter paper and by taking a known quantity of the filtered solution in a crucible of known weight and dried to a temperature of 103^oC-105^oC for un hour and finally the crucible is cooled and weigh with residue.

TDS= (W_1-W_2)/ml of sample x 1000mg/l

Where w_1= weight of empty crucible

W_2= weight of crucible after heating

Determination of sulphate (gravimetric method) (https://www.slideshare.net)

Sulphate is precipitated in a hydrochloric acid medium as barium sulphate by the addition of barium chloride. The precipitation is carried out near the boiling temperature and after a period of digestion the precipitate is filtered and washed with water until free chlorides ignited or dried and weighed as barium sulphate.

Determination of chloride (Argentometric titration) (https://www.slideshare.net)

Chlorides are measured by volumetric procedures employing internal indicators. When water containing chlorides is treated with silver nitrate solution using potassium chromate as an indicator, silver chloride is quantitatively precipitated at a neutral slightly alkaline solution at the end point, red silver chromate is formed.

$$\text{Chloride concentration (mg/l)} = \frac{\text{burette reading}}{\text{Volume of sample (ml)}} \times 1000$$

Determination of TSS (photometric method)

500ml of the sample is blended at a high speed for two hours and poured in to a 600ml beaker then stirred the sample immediately and poured 25ml of the blended sample in to a sample cell and filled a sample cell with 25ml of tap water or deionized water then placed the blank in the cell holder and the light shield closed and the result is taken by the DR-5000 instrument.

Determination of Chromium

Atomic absorption spectrophotometer in the laboratory of Addis Ababa Environmental protection Authority was used to determine chromium (Cr), contents of the sample tannery wastes. The samples were first treated with an acid digestion process and sample solutions were filled up to 100 ml with distlled water after they reached room temperature (it may be filtered through filter paper if necessary). Desired measurements were later done in these obtained solutions by using atomic absorption. The amount of Cr, in the sample wastes were detected with nov AA 400 analytic jena Atomic Absorption Spectrophotometer. Cr was measured at 357.9nm with 0.7 slit intervals by using air plus acetylene (C_2H_2) mixture.

Chapter Four

4. Results and Discussion

4.1. Types and Sources of Tannery Wastes

According to the study made at dire tannery the physical composition of tannery wastes generated during leather manufacturing processes was found to be de-dusted salt, hair waste, fleshing, raw skin trimmings, splitting waste, Pickle trimmings, shavings, Crust Trimmings and leather trimmings and it has been observed from literature review that similar types of solid is generated during manufacturing of finished leather from hides and skins.

In addition to these, sludge and other solid wastes are also generated during tannery wastewater treatment and the main sources of these solid wastes were found to be un-hairing, trimming, fleshing, splitting, which are all carried out in beam house, chrome shaving after chrome tanning operation, crust trimming after re-tanning, finished leather trimming after finishing processes and wastewater treatment plant.

4.2. Generation Rate of dusted salt

Dusted salt is a salt removed by using dome type dodeca wooden frame the wet salted sheep skins and hides before soaking operation. Usually this method of operation is not performed for the purpose of removing the preservative salt. Rather, during unloading of the wet salted sheep skins and hides to the warehouse the salt is get removed from the skin and hides and this de-dusted salt is being disposed along with other types of tannery solid wastes. In order to determine the amount of salt removed from sheep skin, samples of ten pieces of wet salted sheep skins and ten pieces of wet salted hides were randomly taken from the batches prepared for soaking process and each pieces of the samples was weighed using digital balance before and after the method operation to determine the de-dusted salt generated per kilogram of wet salted sheep skins and hides and the results of this experiment are presented in Table 4. as below.

Table 4. The salt generated by desalting hides using dome type Dodeca wooden frame

S.N	Weight of a single piece of wet slated hide before desalting (kg)	Weight of a single piece of wet salted hide after desalting (kg)	Weight of the salt generated from a single piece of hide desalting (kg)	Weight of The salt generated (kg/kg of raw hide)
1	16.220	15.620	0.600	0.037
2	15.820	15.370	0.450	0.028
3	15.340	14.640	0.700	0.045
4	12.550	12.050	0.500	0.039
5	13.440	12.790	0.650	0.048
6	14.110	13.710	0.400	0.028
7	16.110	15.660	0.450	0.027
8	12.330	11.980	0.350	0.028
9	14.720	14.260	0.460	0.031
10	13.500	12.890	0.610	0.045
Average weight (kg)	14.414	13.897	0.517	0.0356

Table 5.The salt generated by desalting skins using dome type Dodeca wooden frame

S.No	Weight of a single piece of slated skin before desalting (kg)	Weight of a single piece of skin after desalting (kg)	Weight of the salt generated from a single piece of skin by desalting (kg)	Weight of The salt generated (kg/kg of raw skin)
1	2.64	2.53	0.11	0.042
2	2.82	2.695	0.125	0.044
3	1.78	1.690	0.09	0.05
4	1.275	1.226	0.049	0.038
5	1.965	1.880	0.085	0.043
6	2.415	2.360	0.055	0.023
7	2.270	2.115	0.155	0.068
8	1.920	1.835	0.085	0.044
9	2.355	2.210	0.145	0.061
10	1.845	1.710	0.135	0.073
Average weight (kg)	2.1285	2.0251	0.1034	0.048

4.2.1. The salt generated after wet salted sheep skins and hides desalting using dome type dodeca wooden frame

Salt preserved sheep skins and hides were used to produce dedusted salt and the salt generated from the beam house operations was determined. In order to determine the weight of a single piece of wet salted sheep skins and hides ten pieces of wet salted samples from each were taken randomly prepared for soaking operation and then each number of pieces of the samples ranging were weighed. The salt obtained using dome type dodeca wooden frame from sheep skins and hides was 4.8% and 3.6% of the total weight of the samples before desalting, respectively. This shows that a tannery having a soaking capacity of 1000Kg wet salted sheep skins and 1000Kg hides is expected to generate 48Kg and 36Kg of salt per day.

4.2.2. Estimations of water and chemicals saved from soaking operations after desalting using dome type Dodeca wooden frame from ten pieces of sheep skins and ten pieces of hides

Table 6. Chemicals used and saved from three soaking operations

Water and chemicals used for soaking operations	Conventional (before desalting)	Using wooden frame (after desalting)	% saved
300%Water for skins(l)	19,156	18,226	4.8
300%Water for hides(l)	43,200	41,400	4.2
0.5%$Ca(OH)_2$for skins(g)	31.9	30.4	4.7
0.5% $Ca(OH)_2$ for hides(g)	216.2	208.5	3.5
0.5% Surfactant for skins(g)	31.9	30.4	4.7
0.5% Surfactant for hides (g)	216.2	208.5	3.5
0.1% Anti fungi for skins (g)	6.4	6.1	4.7
0.1% Anti fungi for hides (g)	43.2	41.7	13.5

During soaking operations 300% water , 0.5% surfactant, 0.5% $Ca(OH)_2$ and 0.1% anti fungi is used based on the weight of wet salted sheep skins and hides. From the above table it can be seen that 4.8% and 4.2% of water from 19,156 liters and 43,200 liters, 4.7% and 3.5% of $Ca(OH)_2$ and surfactant from 31.9g and 216.2g, 4.7% and 3.5% of anti fungi from 6.4g and 43.2g is saved from sheep skins and hides soaking respectively. Since the amount of soaking chemical consumption reduced during soaking of desalted skin/hide the other parameters concentration also reduced by certain amount and the water consumption after desalting minimized volume of waste water generated and discharged from soaking unit operation also reduced this in turn reduce the electric power consumption and chemicals for waste water treatment

Reduction of TDS from soaking operation

Table 7. Effect of desalting on TDS emission from soak yard

	TDS (mg/l)	
TDS emission in soak	**First soak**	**Second soak**
Average TDS of soak liquor without desalting (300% water for soaking)	49,250	25,550
Average TDS of soak liquor after desalting (300% water for soaking)	30,800	13,440
% minimized	37.5	47.4

As can be seen from the above table the total dissolved solid from the soaking operation of sheep skins and hides was minimized by 37.5% and 47.4% respectively by using dome type dodeca wooden frame.

4.3. REUSE OF DUSTED (RECOVERED) SALT IN PICKLING

It is found that 0.0356 kg of salt can be obtained from desalting 1 kg of raw hide and 0.048kg of salt from 1 kg of sheep skin . Dusted salt contains impurities. The chloride content of the solution prepared with dusted salt is less when compared to the solution prepared with fresh common salt.

4.3.1. Clarification of dusted salt solution

The dusted salt is prepared as a 12% solution. The solution is screened to remove hair, tissue, sand and other insoluble matters and the filtrate is treated with poly aluminum chloride (300 mg/l) and poly-electrolyte (2 mg/l) and allowed to settle for 4 to 6 hours.

Table 8. Characteristics of clarified dusted salt solution

#	Parameter	Value
1.	Total dissolved solids	197g/l
2.	Chlorides	108 g/l
3.	Total suspended solids	19 mg/l
4.	Proteolytic bacterial count	9 CFU/ml

4.3.2. Use of dusted salt in pickling

The salt generated by desalting per ton is only 44.5 % hide and 60 % sheep skin of the salt required (i.e. 80 kg per ton of pelt) in pickling. Fresh water and common salt are added, where after the clarified dusted salt solution is mixed in. The drum is run for 5 minutes to dissolve the salt. Salt concentration should be 8^0 Bé. After this stage, diluted (1.5 %) sulphuric acid is slowly added. The drum is then run for 90 minutes and the leather pH checked for 2.8 (UNIDO, 2011). Thereafter the usual chrome tanning operation is followed. Upon completion of the chrome tanning process, the leather was checked for any visible grain damage due to micro-organisms, if any, from the dusted salt. No grain damage was found and the wet blues produced were identical with those processed under the normal procedure.

10 cowhides were taken and cut along the backbone to obtain 20 sides. The left sides were processed by replacing 50% of salt used in pickling with dusted salt. The right sides were processed with fresh common salt. These trials were done in full-scale

production by making marks of identification on the material taken for study. After tanning the sides were assessed. The grain was examined using a microscope and no damage was seen on leathers that were pickled using dusted salt.

4.3.3. The use of supernatant from chrome recovery plant & dusted salt in pickling

Recovery of chrome from spent chrome liquor by the process of precipitation is studied With a view to reduce the use of fresh salt in pickling and conserving water, the supernatant from chrome recovery plants, which is waste liquor, was used for dissolving dusted salt obtained from desalting. The characteristics of supernatant from chrome recovery plant are given in Table 9.

Table 9. Characteristics of supernatant liquor from chrome recovery plant

S.nº	**Parameter**	**Value**
1.	pH	7.7
2.	Chloride as Cl^-	45,100 mg/l
3.	Sulphate as SO_4^{2-}	19,600 mg/l
4.	Chrome as Cr	4 mg/l

With chlorides at about 45 g/l in CRU supernatant, 46 kg of dusted salt was dissolved in a volume of 220 l of supernatant and the solution clarified as described before. After clarification, the solution was found to contain 50 kg of salt – 40 kg from the dusted salt and 10 kg from the supernatant. This was applied to a drum load of 1,000 kg of pelt. In order to reach the required salt concentration of 8^0 Bé, 30 kg of fresh common salt dissolved in 580 l of water was added to the drum. Pickling and chrome tanning were carried out in the usual way there after The wet blue leather was checked for color and hydrothermal stability and found to be of acceptable quality. The grain of the wet blue leather was examined visually and found to be free of bacteria-related damage.

4.4. Determination of the final discharged waste water

The physico-chemical characterization indicates that the chloride content from the general waste water generated before desalting from the tannery was found to be 1560 mg/l which is much higher than the safe limit or Ethiopian EPA standard 1000 mg/l (see annex 3) but the content after desalting was found to be 906.4 mg/l which is below the standard.

Table 10. Determination of the final discharged wastewater for hides and skins

S.nº	parameter	Before desalting	After desalting
1	Chloride(mg/l)	1580	926
2	»	1532	898
3	»	1568	914
4	»	1576	902
5	»	1544	892
average		1560	906.4

Chapter Five

5. Conclusion and Recommendations

5.1. Conclusion

From the study made at DIRE tannery on recycling of dusted salt from raw hides/skins for pickling operation using supernatant (waste liquor) from chrome recovery unit the following conclusions were drawn.

Most of the physical composition of wastes generated from the tannery is found to be de-dusted salt from the beam house process and sludge from the waste water treatment plant. The study on the existing waste disposal of DIRE Tannery indicates that the wastes generated from the tannery is being disposed to the river near to the tannery Therefore, as industrial waste contains hazardous components, it should be managed properly.

In the context of the overall cost of treatment of effluent, particularly, when specific discharge limits for TDS and chloride the removal of surface salt contributes to a significant reduction of eventual treatment cost of TDS. The recovery and reuse of the salt applied in pickling and reuse of supernatant from chrome recovery system will result in reduction of TDS in the combined effluent.

The efficiency of soaking is improved as the loose salt on the surface of the raw stock together with other impurities is removed during desalting. The raw stock is effectively cleaned and rehydrated with reduced number of soakings. This reduces the volume of spent soak liquor leaving the tannery, which in turn results in the reduction of land area for solar evaporation pans for evaporation of highly saline streams of effluent.

Desalting the process water at early stage has a significant importance in reducing the content of the dissolved solid in the effluent so that the waste treatment method is simplified in terms of cost, time, and other related issues.

5.2. Recommendations

Based on the study made at DIRE tannery Private Limited Company, the following recommendations are given.

- Practically oriented training has to be given to the concerned bodies of the tannery on how to implement the Technique applied on this study (source reduction and recycling of dusted salt) to manage the waste generated from tannery.
- The dimensions of the DODECA wooden frame may be adjusted to the average size of raw hides or skins and field conditions and the desalting area should be properly ventilated and the Workers handling the raw material (dusted salt and/or dusted salt solution) should wear protective footwear, facemasks and gloves.
- It is recommended that dusted salt be reused in pickling once it has been clarified. Chemicals such as poly-aluminum chloride and poly-electrolyte can be used to clarify the salt and Care should be taken to ensure the removal of suspended and colloidal impurities.
- There must be waste management division lead by professionals in the organizational structure of tanning industry which has the responsibility of managing wastes generated from the tannery.
- Environmental laws have to be strictly enforced by the federal and regional environmental protection authorities to control improper tannery waste disposal.

References:

Alebel Abebe Belay, 2010, Impacts of Chromium from Tannery Effluent and Evaluation of Alternative Treatment Options, Journal of Environmental Protection, 2010.

Amanial haile reda (2015), Journal of environmental chemistry and Ecotoxicology

Banuraman, S. and Meikandaan, T.P. (2013) Treatability Study of Tannery Effluent by Enhanced Primary Treatment. International Journal of Modern Engineering Research (IJMER), 3(1), 119-122

Belay, W. and Andualem, A. (2008) Cleaner Production for solid waste Management in Leather Industry, Journal of EEA, 25, 1-7.

Bench Marking (Technology Up-gradation) Program in Ethiopian Tanning Industry, Report – Consolidated EMS Report, Prepared by Central Leather Research Institute (CLRI), (Council of Scientific and Industrial Research) Chennai, India October, 2010

Bitton, G. (2005) Wastewater Microbiology, 3rd Edition, John Wiley and Sons, Inc.

Chan, Y.J., Chong, M, F., Law , C.L and Hassel, D.G (2009) A review on anaerobic-aerobic treatment of industrial and municipal wastewater, Chemical engineering Journal, 1-18, ELSEVIER (available on: www.elsevier com/locate/cej).

City of Riverside (2008) Wastewater Collection and Treatment Facilities Integrated Master plan, Volume 4: Wastewater Treatment system, Chapter 6: Primary Treatment, USA.

Conservation strategy of Ethiopia (CSE) (1997), Volume 2: Federal Policy on the Environment, Federal Demokratic Republic of Ethiopia, Addis Ababa, Ethiopia.

Degefu, F., Lakew, A., Tigabu, Y. and Teshome, K. (2013) The Water Quality Degradation of Upper Awash River, Ethiopia. Ethiopian Journal of Environmental Studies and Management, 6(1), 58-66.

Demonstration and propagation of cleaner tanning technologies and improvement of OSH practices & effluent treatment plants, DG/IND/98/213 (Kanpur), December 2000

Dott. Michele Tomaselli 1999, Treating Sludge's and Solid Residues, World Leather,

Durai, G. and Rajasimman., M. (2011) Biological treatment of tannery wastewater-a review journal of Environmental Science and Technology. Asian Network for Scientific Information, 4(1), 1-17.

EPA, 2003,EIA Proclamation number 299/2002. Federal Negarit Gazeta, Federal Demokratic Republic of Ethiopia, Addis Ababa, Ethiopia.

Environmental Pollution Control Proclamation number 300/2002, Federal negarit Gazeta, Federal Demokratic Republic of Ethiopia.

Ethiopian Leather Journal, By Ethiopian Leather Industries Association, March 2012, 6th Edition, page 44

FAO World Statistical Compendium For Raw Hides and Skins, Leather And LeatherFootwear19192009:http://www.fao.rog/fileadmin/templates/est/COMM_MARKETS_M ONITORING/hides skins/documents/AA_ OMPENDIUM_2010.pdf

Federation of Canadian Municipalities and National Reaserch council (FCMNRC) (2003) Wastewater treatment plant Optimization, Canada.

FEPA and UNIDO (2003), Federal Negarit Gazeta, Federal Demokratic Republic of Ethiopia, Addis Ababa, Ethiopia.

Flores-Alsina, X,. Gallego, A., Fejjoo, G. and Rodriguez-Roda, I. (2010) Multi-objective evaluation of wastewater treatment plant control alternatives, Journal of Environmental Management, Elsevier Ltd, 91, 1193-1201.

Flores-Alsina, X,. Rodriguez-Roda, I., Sin, G. and Gernaey, K.V.(2008) Multi- Criteria analysis of wastewater treatment plant control strategies under uncertainity. Wat. Res. 42(17), 4485-4497.

Gebre G. and VanRooijen, D. (2009) urban water pollution and irrigated vegetable farming in Addis Ababa, 34 th WEDC International Conference, Addis Ababa, Ethiopia.

Gebrekidan, A., Gebresellasie, G. and Mulugeta, F. (2009) Environmental impacts of Sheba tannery (Ethiopia) effluents on the surrounding water bodies, Bulletin of the chemical society of Ethiopia 23(2), 269-274.

Getahun, M. and G.Selassie, Y. (2013) Pollution of Water, Soil and Vegetables: Challenges to Growing Cities of Bahir Dar and Kombolcha, Amhara Region. Ethiopia. Journal of Agricultural Science, 5(9), 22-28.

H. Ozgunay, *et al*. Characterization of Leather Industry Wastes, Polish J. of Environ.Stud. Vol. 16, No. 6 (2007), 867-873

Haines B.M., Sykes R.L., Properties of Pickled Hides. *J. Soc. Leather. Tech. Chem.*, **57**, 153-165, 1973. Heidemann E., *Fundamentals of leather manufacturing,* Eduard Roether KG, 197-201, 1993.

Hammer, M, J. and Hammer Jr., M.J. (2001) Water and Wastewater Technology, Prentice Hall of India Private Limited, Fourth Edition, New Delhi, India.

http://en.wikipedia.org/wiki/Waste_hierarch

https://www.slideshare.net

Integrated Pollution Prevention and Control (IPPC), 2000 Reference Document on Best Available Techniques for the Tanning of Hides and Skins, European Commission Directorate-General JRC Joint Research Centre, Institute for Prospective Technological Studies (Seville), Technologies for Sustainable Development, European IPPC Bureau

International Union of Environment (IUE) Commission of the international union of Leather Technologists and Chemists Societies (IULTCS) (1997), typical pollution values related to conventional Tannery Processes, London, UK.

Itanna F. (1998) Metal Concentration of some vegetables irrigated with industrial liquid waste at akaki, Ethiopia Journalof Science, 21(1), 133-144.

K.H. Munz, S. Banaszak *et al*, 2006 Salt-Free Curing of Hides and Skins and Reducing the Salt Content of Tannery Effluents, World Leather, February/March

L.A.H.M. Verheijen D. Wiersema, L.W. Hulshoff Pol, J. De Wit (1996) Livestock and the Environment: Finding a Balance Management of waste from animal product processing, International Agriculture Center, Wageningen, The Netherlands.

Leather international news and technology (2009) free newsletter, best available technologyfor tannery effluent treatment (http://www.leathering.com/featurebest-available-technology-for-tannery-effluent-treatment/).

Liu C.K., Latona N.P., Taylor M.M., Effects of Bating, Pickling and Cross linking Treatments on the Characteristics of Fibrous Networks from Un-tanned Hides. *J. Am. Leather Chem. Assoc.*, **108**, 79-85, 2013.

Lizaridies, N.K., Matis, K.A., Stalidis, G.A., Mavros, P. (1992) Dissolved aie floatation of metal ions. Separation Science and Technology 27, 1743-1758.

Malden Bosnic,UNIDO Consultant in tannery effluent treatment, December,1997.

Melaku, S., Wondimu, T., Dams, R. and Moens, L. (2007) Pollution status of Tinishu Akaki River and its tributaries (Ethiopia) evaluated using physic-chemical parameters, major ions, and nutrients, Bull. Chem. Soc. Ethiop., 21(1), 13-22.

Mersha Z. (2008) Water Quality Monitoring Design for Little Akaki River. Unpublished M.Sc. thesis

Metcalf and Eddy (2003) wastewater engineering: Treatment and reuse, 4th edition, Metcalf and Eddy Inc.

Mwinyikione Mwinyihija (2012) pollution control and remediation of the tanning effluent

Palanisamy, (2000), Recent Trends in Leather Making: Processes, Problems, and Pathways, Critical Reviews in Environmental Science and Technology.

Palanisamy, (2005) Recent Trends in Leather Making: Processes, Problems, and Pathways, Critical Reviews in Environmental Science and Technology,

Rubio, J., Souza, M.L. and Smith, R.W. (2002) Overview of floation as a wastewater treatment technique, Mineral engineering, 15, 139-155 (available on www.elsevier.com/locate/mine).

Society of Leather Technologists and Chemists, Official Methods of Analysis 1996, Northampton, UK

Solid Waste Management Proclamation No. 513/2007, Federal Negarit Gazeta of the Federal Democratic Republic of Ethiopia.

Study on flow of hides and skins in the state of Tamil Nadu and alternate techniques to replace salt curing, Dr. T.J. Devassy, June 1996, UNIDO.

Tare, V., Gupta, Sand Bose, P. (2003) Case studies on biological treatment of tannery effluents in India. Journal of the air and waste management association, 53 (8), 976-982

Tassew, A. (2007) Assesement of Biological Integrity Using Physico-chemical Parameters and Macroinvertebrate Community Index Along Sebeta River, Ethiopia, MSC Thesis, Addis Ababa University, Addis Ababa, Ethiopia.

Terminal report on mechanical desalting and Sulphide reduced liming, CLRI-UNIDO, November 1995

The European Tanning Industry Sustainability Review, Prepared by COTANCE as a contribution to the World Summit on Sustainable Development, May 2002

UNEP (1996) Cleaner Production in Leather Tanning, A Workbook for Tanneries, first edition, France.

UNIDO (2001) regional program for pollution control in the tanning industry in south East Asia

UNIDO (2011) Introduction to Treatment of Tannery Effluents: What every tanner should know about effluent treatment, Vienna.

V. Suresh, M. Kanthimathi *et al.* An Improved Product-Process for Cleaner Chrome Tanning in Leather Processing, Journal Of Cleaner Production 9 (2001) 483–491

Vochten, P., Schowanec, S., Schowanec, W and Verstraete, W. (1988) Aerobic versus anaerobic wastewater treatment, Proc. Of the 5th Int. Symp. On Anaerobic Digestion, Bologna, Italy. Hall , E., R. and Hobson, P.N. (Eds.), Pergamon Press, UK, 91-104.

Von Sperling, M, (1996) Comparision Among the most frequently used systems for wastewater treatment in developing countries, Water Science and Technology, Elsevier Science Ltd, 33(3), 59-72.

Wei X.Y., Zhang W.H., Shi B., Effect of Neutral Salts on Pickling and Tanning – a Study Based on Assembly Behavior of Collagen. *J. Soc. Leather. Tech. Chem.*, **98**, 30-34, 2014.

WHO and UNEP (1997) Water Pollution Control-A Guide to use of water quality Management Principles.

World Bank Group (2007) Environmental, Health Safety Guidelines for Tanning and Leather Finishing.

Zeleke, A. (2011) Tannery wastewater management problems in Ethiopia, MSC Thesis, Electronic Thesis and Dissertations Digital Library, Addis Ababa University. (http://hdl.handle.net/123456789/4168).

Zeleke, A., Seyoum, M. and seyoum, L. (2010) Assesement of water pollution and Biological Intigrity Along Modjo River, Ethiopia Using Macroinvertebrate Metrics and Physico chemical Parameters, presented on a conference on Water resources in Ethiopia, A.A., Ethiopia.

Zulfikar, A. (2012) Assessment of Tannery Solid Waste Management and Characterization: A Case OF Ethio-Leather Industry Private Limited Company (ELICO), MSC Thesis in Environmental Engineering, Addis Ababa University, Addis Ababa, Ethiopia.

Annexes

Annex 1: Daily soaking capacity of Tanning Industries

	Name of tanneries	Soaking Capacity(pieces/day)		Soaking Capacity (tonne/day)	
		Skin	Hide	Skin	Hide
1	Ethiopia Tannery Share	14500	1300	21.75	33.28
2	Dire Tannery	6000	600	9	15.36
3	Hafde Tannery Plc	9000	500	13.5	12.8
4	Wallia Tannery Plc	7000	300	10.5	7.68
5	Batu Tannery Plc	3000	700	4.5	17.92
6	Modjo Tannery Share Company	5700	200	8.55	5.12
7	ELICO	15000	800	22.5	20.48
8	Bahir Dar Tannery Plc	3000	100	4.5	2.56
9	Blue Nile Tannery	5000	0	7.5	0
10	Debrebrehan Tannery	6500	0	9.7	0
11	Addis Ababa Tannery	900	0	1.35	0
12	Sheba Tannery	6000	300	9	7.68
13	Kolba Tannery Plc	9000	400	13.5	10.24
14	Mersa Tannery Plc	10000	500	15	12.8
15	Bale Tannery Plc	0	600	0	15.36
16	Kombolcha Tannery	5000	0	7.5	0
17	Hora Tannery Plc	4700	0	7.05	0
18	Gellan Tannery PLc	4000	0	6	0
19	Dessie Tannery Plc	5000	0	7.5	0
20	Abay Tannery PLc	4000	0	6	0
21	Mesaco Global Tannery	3000	0	4.5	0
22	Shoa Tannery Plc	6000	500	9	12.8
23	Crystal Tannery	7000	1000	10.5	25.6
24	China Africa Tannery	8224	0	12.336	0
Total		147524	7800	221.24	199.7

Annex 2: wet salted hides and skins in dire tannery

Annex 3: Emissions Limits of tanneries waste water

Emission (mg/l)	Ethiopian EPA standard
BOD_5	200
T-N (as N)	60
TDS	500
TSS	50
Cr (as total Cr)	2
COD	500
Cl^-	1000
Total ammonia (as-N)	30
Total phosphorus (as N)	10
Sulphide (as S)	0.1

Annex 4 Digital material balance

Annex 5 Finished sheep skin and hide leather using dusted salt

Finished sheep skin leather

Finished hide leather

Annex-6 Automatic drum