2020-02

Treatment of Tannery Soaking Wastewater Using Advanced Electro Oxidation

Abera, Mekdes

---

http://hdl.handle.net/123456789/10923

BAHIR DAR UNIVERSITY
BAHIR DAR INSTITUTE OF TECHNOLOGY
SCHOOL OF RESEARCH AND GRADUATE STUDIES
FACULTY OF CHEMICAL AND FOOD ENGINEERING

Wisdom at the source of the Blue Nile

TREATMENT OF TANNERY SOAKING WASTEWATER USING ADVANCED ELECTRO OXIDATION

BY

MEKDES ABERA ABOYE

BAHIR DAR, ETHIOPIA
FEBRUARY, 2020

Wisdom at the source of the Blue Nile

TREATMENT OF TANNERY SOAKING WASTEWATER USING ADVANCED ELECTRO OXIDATION

Mekdes Abera Aboye

A Thesis
Submitted to the School of Graduate Studies of Bahir Dar university Institute of technology;
in partial fulfillment of the requiremnts for the degree
Of
Master of science in Chemical Engineering (Environmental Engineering Stream) in the
Faculty of Chemical and Food Engineering.

Advisor: Nigus Gabbiye (Phd)

Bahir Dar, Ethiopia
Feburuary, 2020

DECLARATION

This is to certify that this thesis entitled with- Treatment of Tannery Soaking Wastewater Using Advanced Electro Oxidation, submitted in partial fulfillment of the requirements for the award of Master of Science in environmental engineering to the Graduate Program faculty of food and chemical engineering, Bahir Dar University by Mrs. Mekdes Abera Aboye who is an authentic work carried out by herself under our guidance. The matter embodied in this project work has not been submitted earlier for award of any degree or diploma to the best of our knowledge and belief.

Mekdes Abera 03/03/20
Name of the Student Signature Date

Nigus Gabbiye 08/07/2020
Name of the Advisor Signature Date

Bahir Dar University

Bahir Dar Institute of Technology

School of Research and Grauate Studies

Faculty of Chemical and Food Engineering

THESIS APPROVAL SHEET

Name **Signature** **Date**

Mekdes Abera 03/03/20

The following graduate faculty members certify that this student successfully presented the necessary written final thesis and oral presentation for partial fulfillment of the thesis requirements for the award of the degree of Master of Sciences in Chemical Engineering (Environmental Engineering).

Board of Examiners

Name of Adviser Signature Date

Nigus Gabbiye 08/07/2012

Name of External Examiner Signature Date

Dr. Kibret Yilma 03/03/20

Name of Internal Examiner Signature Date

Elias Wagari (PhD) 08/07/2012

Name of Chair Person Signature Date

Elias Wagari (PhD) 08/07/2012

Faculty Dean Signature Date

Ali Seid /07/12

ACKNOWLEDGE

This study would not have been possible without the mercy of our Heavenly Father, who gave me the strength, courage and perseverance to complete this study.

I want to forward my deep thanks to my advisors Dr. Nigus Gabbiye for his support and guidance without him this study would have been difficult.

I am extremely thankful to my friend, Wintana Kasahun, for her encouragement and endless support. Special thanks go to Maerge Haile for her positive support during lab work. My thanks are also addressed to Bethlehem Tegegn, Marta Taye and Yodit Taddese for their support.

I would like to thank leather industry development institute (LIDI), for their support during my study. I would like to thank also my family for his encouragement and support. It is not easy to name all others who supported me, I thank them all.

ABSTRACT

Skins/ hides are transformed into leather through many complex stages, consuming high quantities of water and using large amounts of chemicals. The leather tanning industry has been identified as one of the main causes of environmental pollution in Ethiopia. In general, tannery wastewaters have a dark brown and have a high content of organic substances that vary according to the chemicals used. Soaking wastewater have more of high organic and NaCl.

Tanneries in Ethiopia generate large amount of soak wastewater and discharge to the surrounding environment with partial treatment sometimes without any treatment and cause environmental pollution and public health problem.

Soak liquor, a primary effluent from the tannery industry has contain high organic load (flesh, skin, blood, humic substances and other suspended particles) and sodium chloride (salt), making a challenge for the conventional treatment technologies.

An electro oxidation wastewater treatment method was investigated to treat tannery waste liquor for the effective discharge of the final effluent. A series of batch electro oxidation experiments for a wide range of contact time (30 – 120 minutes), different salt concentration (13.5g/L – 15 g/L) and at a current density of 0.012A/cm^2 were performed for the effective removal of the liquor waste. Optimal removal efficiency of 85.86%, and 84.31% and 12.51% of COD, BOD and TDS respectively were recorded over the factors level of a contact time of 120 minutes, and at pH of 8 and 9. Highest reduction in COD and BOD were observed as 84.4 % and 84.06 % at salt concentration of 15 g/L.

The present study claims that the process of EO gives better performance on reduction of COD and BOD while comparing previous studies.

Keywords: Tannery, Soaking Liquor, Electro oxidation, wastewater

TABLE OF CONTENTS

ACRONYMS .... **IX**

LIST OF FIGURES .... **X**

LIST OF TABLES .... **XI**

CHAPTER ONE **1**

1. INTRODUCTION 1

1.1 Background of the study *1*

1.2 Statement of the Problems *2*

1.3 Objectives *3*

_1.3.1 GENERAL OBJECTIVE 3

1.4 Significant of the study *4*

CHAPTER TWO **5**

2. LITERATURE REVIEW 5

2.1 Introduction *5*

2.2 Leather Processing and Wastes *6*

2.3. Types of Wastes Generating in Tannery *10*

2.4 Wastewater Treatment *11*

2.5 Physico-Chemical Treatment System *11*

2.8 Mechanism of electrochemical oxidation *24*

CHAPTER THREE **27**

3. MATERIALS AND METHODS 27

3.1 Materials *27*

3.1.1 Raw materials and Reagent *27*

3.1.2 Equipment *27*

3.2 Methods *28*

3.2.1 Sample Collection and Preparations *28*

3.2.2 Experimental set-up *29*

3.2.3 Analysis and Characterization of Wastewater *30*

3.3 Statistical Analysis *35*

CHAPTER FOUR **36**

4. RESULTS AND DISCUSSION 36

4.1 Characteristics of Raw Soaking Wastewater *36*

4.1.1. Characteristics of Treated Soaking Wastewater *37*

CHAPTER FIVE **47**

5. CONCLUSION AND RECOMMENDATION 47

5.1 Conclusion *47*

5.2 Recommendation *47*

REFERENCE **49**

ANNEX **57**

ANNEX 1: DAILY SOAKING CAPACITY OF ETHIOPIAN LEATHER INDUSTRIES 57

ANNEXES II: LABORATORY PROCEDURES FOR WATER AND WASTEWATER ANALYSIS. 58

ANNEXES III: MODEL SUMMARY STATISTICS 62

ANNEXES IV: APPEARANCE AND FACTORS OF ELECTRO-OXIDATION FOR TREATMENT 65

ANNEXES V: EFFECT OF DIFFERENT PARAMETERS ON WASTEWATER PARAMETER (COD, BOD & TDS 67

ACRONYMS

APHA	American Public Health Association
AOP	Advance Oxidation Processes
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
Cr (VI)	Chromium (VI)
TDS	Total Dissolved Solid
SS	Suspended Solid
SBR	Sequencing Batch Reactor
S^{2-}	Sulphides
NaCl	Sodium Chloride
LIDI	Leather Industry development Institute
UNIDO	United Nations Industrial Development Organization
UNEP	United Nations Environment Program

List of Figures

Figure 1.1 Process flow sheet diagram 2

Figure1.2 in flow and out flow of Tanning Industry. 6

Figure 2.1 Electro Oxidation Wastewater Treatment Systems 23

Figure 3.1 Setup of the lab-scale electro oxidative reactor...29

Figure 3.2 COD Measurment..29

Figure 3.3 BOD incubator...29

Figure 3.4 TDS Measurment...29

Figure 3.5 Experimental Setup of the lab-scale electro oxidative reactor 29

Figure 3.6 Characterization of the raw and treated effluent 35

Figure 4.1 Effect of pH on COD, BOD During electro oxidation salt concentration 14000mg/L...39

Figure 4.2 the parameter of the pollution of waste water before and after treated............................39

Figure 4.3 Effect of pH with electro-oxidation time on COD reduction with the salt concentration 15g of NaCl/L. 44

Figure 4.4 pH of different tanning processes..45

Figure 4.5 Biological oxygen demand at different processes of leather stage...................................45

Figure 4.6 Chemical oxygen demands at different processes of the leather stage. 45

Figure 4.7 the profile of variation (a) pH and (b) COD, with time during Electro –oxidation at room temperature 46

List of Tables

Table 2.1 Legal ranges of selected parameters 8

Table 2.2 Cleaner Technological Options and its Advantages 9

Table 3.1 Experimental factors and levels 33

Table c.1 the Experimental design and predicted response for wastewater of EO 33

Table 4.1 Raw soaking liqour Physico-chemical quality 36

Table 4.2 Characterstics of soaking wastewater after treatment through electro-oxidation at salt concentration of 13,500 mg L^{-1} 37

Table 4.3 Characteristics of soaking wastewater after treatment through electro-oxidation at salt concentration of 14,000 mg L^{-1} 38

Table 4.4 Characteristics of soaking wastewater after treatment through electro-oxidation at salt concentration of 15,000 mg L^{-1} 39

Table 4.5 Characteristics of soaking wastewater after treatment through electro-oxidation at pH of 7 40

Table 4.6 Characteristics of soaking wastewater after treatment through electro-oxidation at pH of 8 40

Table 4.7 Characteristics of soaking wastewater after treatment through electro-oxidation at pH of 9 40

Chapter one

1. Introduction

1.1 Background of the study

Leather manufacturing sector in Ethiopia is one of the priority sectors due to the availability of resources for leather manufacturing, its potential for export market, for generating massive employment opportunities. The leather industry generally uses hides and skins as raw materials, which are the by-products of meat processing industry. In this respect, the leather industry could have easily been distinguished as an environmentally friendly industry; since it processes waste products from meat production. However, the leather industry has commonly been regarded as a polluting industry due to the bad smell, high discharge of organic and inorganic wastes and high-water consumption caused during traditional manufacturing processes. Leather is animal skin that has been chemically modified to produce a strong, flexible material that resists decay. Almost all the world output of leather is produced from cattle hides, goat skins and sheep skins.

Currently there are 31 tanneries in Ethiopia of which 27 are in operation and most of them are located in vicinity of Addis Ababa. Annually, all leather industries put together use 2.3 million pieces of hides and 44.3 million pieces of skins as an input for processing at full capacity operations. According to the Central State Agency of Ethiopia, in 2012/13 Ethiopia has a livestock population consisting of 53.99 million cattle, 25.5 million sheep, 24.06 million goats, 1.91 million horse and 0.92 million camels. The existing daily soaking capacity of tanning industries is 141,500 pieces of skins and 9,050 pieces of hides (See Annex 1).

Leather industry has been categorized as one of the highly polluting industries and there are concerns that leather making activity can have adverse impact on the environment. Wastewater generated in leather industries contribute mainly from beam house, tanning, and finishing section. Almost all tanneries in Ethiopia has no clean leather manufacturing technology, all types of generated wastewater dumped in to the surrounding environment.

The sustainability of the leather industry crucially depends on how well it manages the liquid and solid wastes. While end-of-pipe treatment systems are in place to comply with discharge standards for liquids, solid waste management is becoming critical.

Leather industry in the developing countries is facing lots of wastewater problem. Tannery generates huge amount of wastewater which has different effluent chemicals such as liming, sulfide, organic salts and other healthy and environmental affecting chemicals. Different forms of waste in quantity and quality, which emerge during transformation of hides and skins to leather, have negative impacts on the environment.

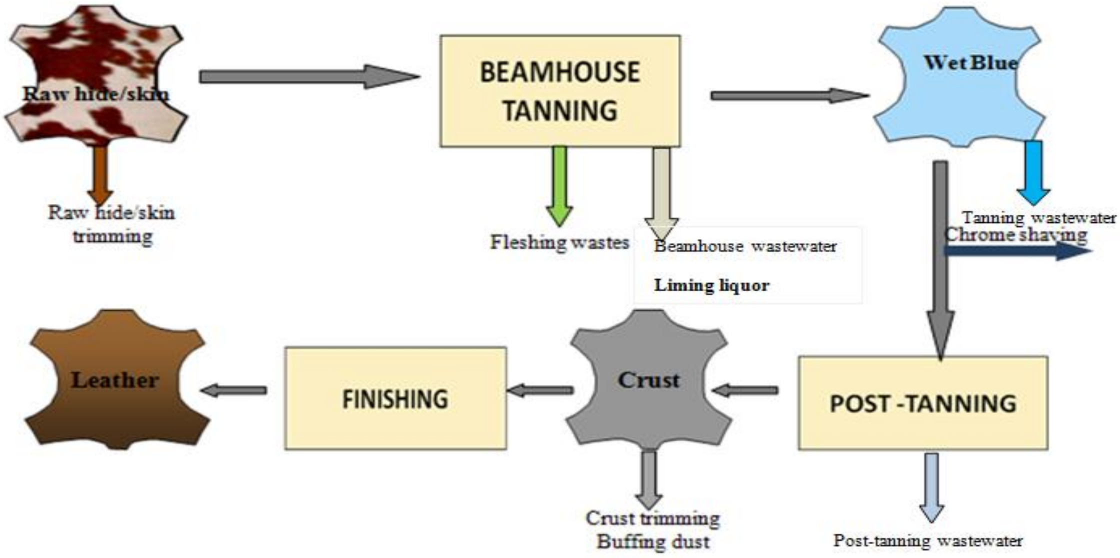

Figure 1.1 Process flow sheet diagram

The transformation of hide or skin into leather utilizes many chemical and mechanical processes and generates solid and wastewater

1.2 Statement of the Problems

The operation of tannery industries in Ethiopia is causing severe environmental degradation due to the disposal of untreated influent on land and in water bodies. About 130 different types of chemicals are applied in leather manufacturing.

The improper management of tannery wastewater is one of the environmental challenges facing urban cities worldwide with particular emphasis on developing countries, like any other developing country here in Ethiopia society faces the same problem. Wastewater generated from leather manufacturing industries dumped into river and environment, no attention is given to waste management practices as loads of wastes are dumped indiscriminately in open dumps into rivers and canals.

Wastewater from leather production is known to be heavily loaded with numerous contaminants, which cause series pollution for aquatic organisms, hazardous public health, and a serious threat to the environment.

Soaking wastewater from tannery waste can cause immense effects not only to the environment but also to the human health. This has contributed to the spread of communicable diseases in the affected areas.

The large volume of wastewater has been generated at the soaking process. Soak liquor, a primary effluent from the tannery industry has intense brown color, hyper salinity, and stinky odor. Soaking wastewater has high impact on the influent treatment plant due to organic pollutants and a high concentration of salt. The wastewater of soaking is composed of 2-4 % of sodium chloride and organic contaminants (flesh, skin, blood, humic substances and other suspended particles). If this effluent is discharged into nearby lands without any prior treatment, it will pollute the lands and groundwater. So, to solve those problems the soaking wastewater can be treated with electro – oxidation to reduce the TDS, COD and BOD by the degradation of the organic pollutant and using the salt as the catalyst for the electrochemical oxidation process.

Therefore, this study helps to realize clean, reuse the treated wastewater for further application such as leather processing, watering garden, and cleaning operations. Since the project is cost-effective it applies to industrial zones and factory levels wherever they are available.

1.3 Objectives

1.3.1 General Objective

The main objective of this study is to investigate the treatment of tannery soaking wastewater using advanced electro oxidation mechanism for the effective treatment of large volume of soaking liquor

1.3.2 Specific Objective

The specific objectives of the study are:

- To characterize the physical and chemical properties of the effluent soaking wastewater.
- To investigate the effect of operating conditions (Solution pH, Salt concentration and contact time) on the Electrochemical -oxidation performance of soaking waste liquor.

- To evaluate and characterize the treated wastewater quality and compare it with the Ethiopia wastewater quality standard.

1.4 Significant of the study

- The research is applicable to any firms/ tannery due to its simple. wastewater treating technology
- Less cost of water treatment and easy to reduce Environmental Pollution
- Treated wastewater that complies with Ethiopia environmental standard.
- The water consumption in leather industries can be minimized significantly by adopting this technique.
- This method effectively to reduces the environmental pollution

Chapter Two

2. Literature Review

2.1 Introduction

The water consumption and effluent disposal in the leather industry is considered as a serious environmental threat. About 85% of fresh water used in leather processing, is disposed of as wastewater, carrying dissolved and suspended chemicals and other substances used in the process, creating serious pollution problems [1]. There are four operating processes applied to leather until it becomes a final product, these are; pre-tanning operation (Beam House Operation), tanning operation, wet- finishing operation and finishing operation. Every tanning step, with exception of the crust finishing operations, produces wastewater. An average of 35 m3of wastewater is produced per ton of raw hide [2].

This wastewater contains: salts (NaCl), fat, protein, preservatives from soaking; lime, ammonium salts, ammonia, protein (hair), and sulphides from fleshing, trimming, bating steps; chromium (salts) and poly phenolic compounds from tanning; and dye and solvent chemicals from wet-finishing step. Toxic effects of tannery waste were caused by the presence of toxic chemicals such as sulphides, chromates and other tanning agents that may interfere biological waste treatment. Toxic discharges retard the process of self-purification and sometimes may cause the death of aquatic life [3]. It is important to determine the principal impurities in the effluent and to pretreat these impurities as necessary step before being released to the sewer, river or lakes.

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. The simplified inflow and out flow of tanning industry is shown in Figure 2.1 below.

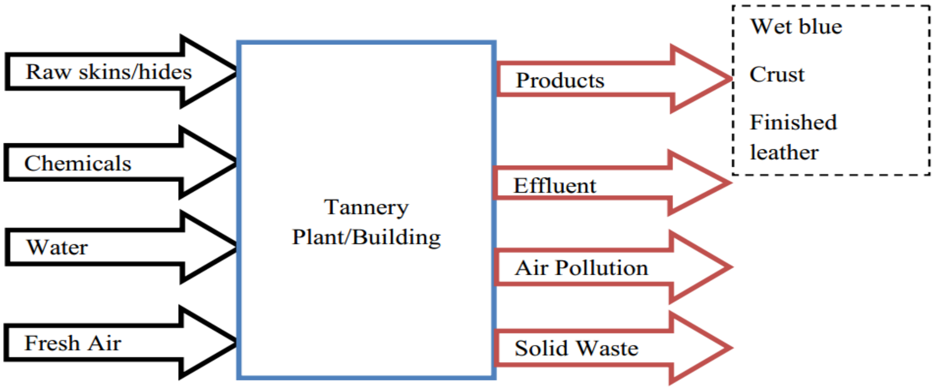

Figure 1.1 in flow and out flow of Tanning Industry

2.2 Leather Processing and Wastes

The manufacturing of leather can be divided in to four parts [6];

i. **Beam house operations**

The term beam house refers to the process in the tannery between the removal of the skins or hides from storage and their preparation for tanning. In beam house operations, the removal of dirt and blood by washing is the first step after which the hides are then soaked in water for softening and removal of salts. After the removal of salts, fatty tissue is removed by fleshing. Liming is done to swell the hides for the better penetration of tanning agents and hair removal. Chemical dissolution of the hair and epidermis is with an alkaline medium of sulphide and lime takes place. During liming, a high concentration of sodium sulphide, lime and organic matter is delivered to the effluent. Hides are then neutralized with acid ammonium salts and treated with enzymes to remove the hair remnants and to degrade proteins. This results in a major part of the ammonium load in the effluent. Pickling is usually done to prepare the hides for tanning. The pH value of hides is adjusted by addition of acids (main sulphuric acid). Salts are added to prevent the hides from swelling.

ii. **Tanning process**

Tanning is the reaction of the collagen fibers in the hides with tannins, chromium, alum or other chemical agents. Alums, syntans, formaldehyde, glutaraldehyde and heavy oils are used as tanning agents. During the tanning process, about 300 kg chemicals are added per ton of hides. Based on the tanning agents, tanning operations are further divided in to vegetable tanning and chrome tanning.

iii. **Post tanning process**

At post-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.

The process of chemical can be performed after tanning but prior to finishing such as neutralization, dyeing, retanning and fat liquoring are called post-tanning or wet finishing operation. The main objectives of this set of unit operations are to give a colour to the leather as demanded by the market (dyeing), impart softness (fat liquoring) and fullness and uniformity of substance start from the wet and produce different types of finished leathers without having knowledge about the beam house and tanning operations the leather had undergone

iv. Finishing operation

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.

The leather tanning and finishing industry has high water consumption and, respectively, generates great amounts of wastewaters with a very complex composition, large quantities of solids and organic material, nitrogen, salts, in addition to some specific pollutants such as chromium and sulphide. Wastewaters generated by tannery industries are known to contain large amounts of potentially toxic wastewaters containing both organic and inorganic compounds. Tanneries effluents are also characterized by high wastewater generation in the range of 30–35 L Kg1 skin/hides process with a variable pH, high concentration of suspended solid, BOD, chromium, COD, and sulfides as well as low biodegradability.

Soak liquor, a primary effluent from the tannery industry has an intense brown colour, hyper salinity, and stinky odour. Soak liquor is composed of 2–4% sodium chloride by weight and contains traces of calcium chloride along with organic contaminants (flesh, skin, blood, humic substances and other suspended particles) such as nitrogen and phosphorous containing compounds. [4, 5]

If this effluent is discharged into nearby lands without any prior treatment, it will pollute the lands and groundwater. Figure 2.2 below shows the leather manufacturing process flow and waste generation.

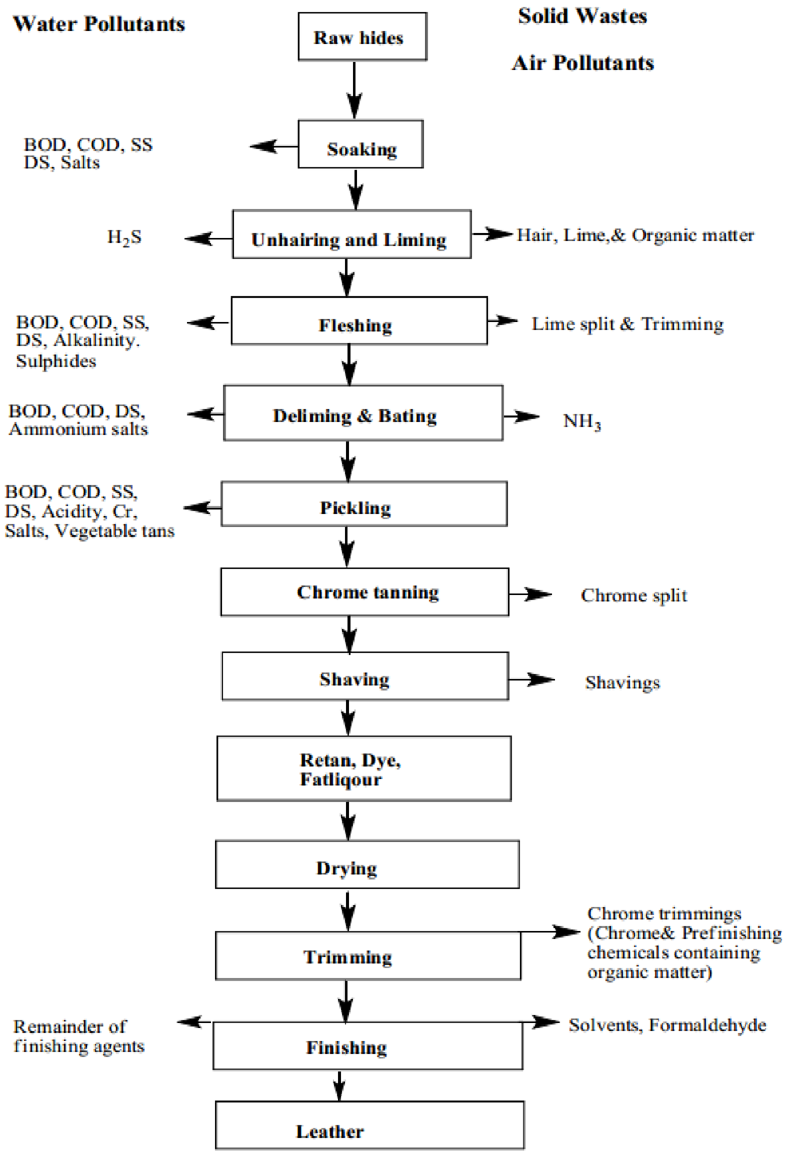

Figure 2.2: Wastes generated from each unit operation of a tannery [7]

An average of 30– 35 m^3 of wastewater is produced per ton of raw hide. However, wastewater production varies in wide range (10–100 m^3per ton hide) depending on the raw material, the finishing product and the production processes [8]. Organic pollutants (protein and lipidic components) are originated from skins (it is calculated that the raw skin has 30% loss of organic material during the working cycle) or they are introduced during processes. The parameters of tannery effluent were found to be high and exceeding the legal ranges of selected parameters discharge to inland water and to sewer (Table 2.1) [9].

Table 2.1 Legal ranges of selected parameters [7]

Parameter	Direct discharge to inland water	Discharge to sewer
pH	**5.0- 10.0**	**5.0- 10.0**
Temperature (^{o}C)	**25-40**	**30-40**
Settl. Solids (mg/l)	**0.3- 1.0**	
BOD5 (mg/l)	**5- 200**	**125- 1000**
COD (mg/l)	**50-450**	**300- 3000**
SS (mg/l)	**20-200**	**75-1000**
Sulfide (mg/l)	**Nil- 10.0**	**Nil- 10.0**
Cr III	**0.1- 5.0**	**1.0- 10**
Cr VI (mg/l)	**Nilhil-1.0**	**Nilhil-1.0**
Oil & grease (mg/l)	**2.5- 100**	**30-500**
Phenols (mg/l)	**0.05-5.0**	**1.0- 90**
Chlorides (mg/l)	**200- 4000**	**400- 600**
Sulfates (mg/l)	**150- 1000**	**300- 400**
TKN (mg/l)	**3- 10**	

The difficulty in treatment of tannery wastewater is due to complex nature of the industry and a large number of chemicals employed in the leather processing. The segregation of each sectional stream and separate treatment therefore requires very high investments in terms of equipment, land etc. hence eliminating or reducing the wastage at the source i.e. at the stage of leather processing, is a promising option for the tanneries. So, me of cleaner technological options are discussed in Table 2.2 [10]

Table 2.2 Cleaner Technological Options and its Advantages

Cleaner technology option	Impact on pollution load
Salt free hide and skin preservation	Helps eliminate salt and reduce TDS
Mechanical desalting	Helps eliminate salt and reduce TDS
Counter current soaking	Reduced water consumption
Enzyme assisted soaking	Reduced water consumption and processing time
Green fleshing	Reduced chemical consumption and solid waste
Enzymatic sulfide free unhairing	Reduced concentration of sulfides, COD, etc in the effluent
Liming splitting	Reduced chemical consumption and solid waste
Hair saving unhairing-liming	Reduced concentration of nitrogen, BOD, COD etc in effluent

Direct recycling of liming floats	Reduced chemical and water consumption and reduced BOD, COD and sulfides in effluent
Ammonia free deliming using carbon dioxide	Reduced nitrogen concentration in the effluent
Chrome recovery, high chrome exhaustion and/or chrome liquor recycles	Reduce concentration of chromium in the effluent

2.3. Types of Wastes Generating in Tannery

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 [11].

2.3.1. Liquid and Gaseous Waste

Tannery effluents are ranked as the highest pollutants among all industrial wastes [12]. 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. 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 is not absorbed in the production process and is discharged in to the environment [13]. 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 m3 per year [9]. On average 45 -50 m3 of wastewater is discharged from tanning industry per ton of raw hide processed [10].

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.) [14].

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 odour [15].

Emissions to air have effect beyond the tannery site, but also affect the workplace and possibly the health of the tannery workforce. Apart from odors, particular mention should be made hereof organic solvent emissions, aerosols and dust (buffing dust and powdery chemicals) [15].

2.3.2. Solid Wastes

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 [15]. 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 [14].

2.4 Wastewater Treatment

The conventional wastewater treatment, usually applied to the mixture of effluents from all production processes, makes use of solids separation and biological treatment. The conventional biological treatment does not always achieve satisfactory performance due to the toxicity of the tannery wastewater that affects the development of the bacteria. In addition, traditional physical–chemical processes are comparatively expensive, and may lead to secondary pollution. This is because it needs additional chemicals.

The drawbacks mentioned above have forced various industries to seek for effective alternative treatment technologies for pollutants removal, ideally by electrochemical methods. Nowadays, electrochemical treatment methods have reached such a state that they are not only comparable with other technologies in terms of cost, but they are also more efficient and more effective.

2.5 Physico-Chemical Treatment System

The physico-chemical treatment of organic effluent consists of adsorption, coagulation, precipitation, flocculation, sedimentation, filtration, ion exchange and chemical oxidation [17 – 20]. Oxidative degradation by chlorine and ozone are the most common chemical processes for color removal. The chlorination however has the disadvantage of producing organochloride byproducts. Coagulation/ flocculation have been tried for leather effluent treatment to reduce COD and suspended solids [21]. Some authors attempted both physical and chemical or combination of both for treating leather industrial effluent to reduce organic pollutant and nitrogenous compound 16 present in the leather effluent [22 – 25]. The ammonia present in the tanning effluent can be removed using adsorption, chemical precipitation, membrane filtration and reverse osmosis [26 – 29]. While the chromium present in the tannery effluent can be reduced by chemical precipitation, adsorption, and ion exchange. The other contributors on physico-chemical methods of tannery effluent treatment are due to the conventional method which includes membrane filtration and coagulation, adsorption, ion exchange. Though the physicochemical methods can be used for removal of both organic and inorganic matter, they are expensive, consume large amount of chemicals and produces secondary solid sludge [30].

2.5.1 Biochemical Method

In this treatment technique, micro-organisms utilize the organic matter for metabolism processes as they can uptake organic matter and nutrients (nitrogen and phosphorus) for energy source [30 – 33]. The biological treatment methods have following advantages : (i) Low capital and operating costs (ii) Relatively less secondary sludge compared chemical method (iii) Eco friendly 17 (iv) Oxidation of a wide variety of organic compounds (v) Removal of reduced inorganic (vi) Operational flexibility to handle a wide range of flows and wastewater characteristics (vii) Reduction of aquatic toxicity Typical biological treatment processes make use of trickling filters, activated sludge, Sequencing Batch Reactor (SBR) and wetland as polishing system.

Organic pollutants and colloidal organics from wastewater can successfully be removed by biological treatments. Biodegradation of organic matter during wastewater treatments occur either in the presence of oxygen (aerobically) or in anoxic conditions [34 – 36]. Several studies focused on bio-remediation of tannery effluents [37 – 38]. Carbon dioxide is generated along with solid sludge when soluble organics are oxidized biochemically. However, the oxidation of organic matter in anoxic environment by denitrification of nitrate or nitrite yields carbon dioxide, water, nitrogen and sludge [39 – 40]. Experimentally proved the possibilities of treating tannery effluent using enzymes, The authors used the combination of hydrolytic enzymes, viz. proteases, carbohydrates, and lipases for treating tanning effluent and suggested that the protein by-product suitable for animal feed as well as energy conservation and fat recovery. Removal of organic pollutant from tannery effluents is clearly favored by the combination of processes with and without oxygen. Microorganisms such as A. fumigate and species of Pseudomonas can reduce the chromium presence in the tanning effluent and P. aeruginosa could be used successfully to degrade pentachlorophenol [41]. Many investigators have reported the use of biological treatments, specifically, sequencing batch reactors (SBR) in tannery wastewater as an efficient way for the removal of organic matter [42 – 44]. The presence of higher concentration hinders the performance of aerobic biological treatment [45]. Even though the conventional methodologies are technically feasible, on lab scale operations they are questionable for their technical and economic feasibility in large scale operations. Thus, it can be observed that the problem involving the proper management of the tannery effluent has not been solved.

2.5.2 Membrane Process

The development of cellulose acetate membranes in the early 1960’s started gaining attention among researchers/industries in 70’s. Today the importance of membrane is felt beyond reverse osmosis (desalination) to wide variety of wastewater treatment applications [46 – 47]. Membrane based processes offer a cleaner technology in the treatment of various industrial processes for separation, purification, concentration, and fractionation of the solutes [48 – 51].

Several advantages of the RO process that make it particularly attractive for dilute aqueous wastewater treatment include: Simple in

- Design and operation, low maintenance
- RO can be used to remove inorganic and organic pollutants simultaneously
- The RO treated effluent can be reused

RO process considerably reduces the volume of waste streams so that the stream can be further treated effectively by other processes such as incineration [51 – 56]. In addition, RO systems can replace or be used in conjunction with other treatment processes such as oxidation, adsorption, stripping, or biological treatment (as well as many others) to produce high quality treated water which can be reused or discharged. Sourirajan and Matsuura (1985) have compiled separation and flux data of cellulose acetate membranes for a large number of organic compounds, including many organic pollutants.

2.5.3 Advance Oxidation Process

Biological methods of treating industrial effluents are suited for easily degradable organics only. However, these methods become ineffective for the effluents containing refractory (resistant to biological treatment) organic pollutants. Advanced oxidation processes (AOPs) have been developed to overcome this problem [57]. In AOP, high powerful oxidants such as ozone, hydrogen peroxide, hydroxyl radicals, and fenton oxygen are generated through different techniques. The oxidant radicals are very reactive and attack the organic molecules with very high rate constants [58]. Further, the oxidants are characterized by a low selectivity which is a useful attribute for an oxidant used in wastewater treatment and to solve pollution problems. The versatility of AOP is also enhanced by the fact that they offer different possible ways for oxidant production thus allowing a better compliance with the specific treatment requirements. Advanced oxidation processes (AOPs) are emerging and promising technology both as an alternative treatment to conventional wastewater treatment methods and enhancement of current biological treatment methods especially dealing with highly toxic and low biodegradable 20 wastes [59 – 60]. The AOPs are attractive alternative for the treatment of refractive organic effluents such as aromatics, tanneries, pesticides, petroleum constituents and volatile organics etc. [61 – 65]. The higher molecule pollutants are reduced to water, carbon dioxide and salts.

The oxidation of organic pollutants with strong oxidants (H_2O_2, O_3 etc.) takes place generally at room temperature. In order to increase the efficiency of mineralization, the oxidation takes place in the presence of catalyst and UV radiation. This technology is interesting for the treatment of dilute wastewater with COD < 5,000 ppm. Although AOP use different reacting systems, but they are characterized by the same chemical feature: production of OH radicals. These radicals are extraordinarily reactive species; they attach the most part of organic molecules with very high rate [58].

OH, radicals are also characterized by a low selectivity of attach which is a useful attribute for an oxidant used in wastewater treatment and to solve pollution problems. The versatility of AOP is also enhanced by the fact that they offer different possible ways for OH radical production thus allowing a better compliance with the specific treatment requirements. AOP are usually classified according to the reaction phase (homogeneous or heterogeneous) or to the OH radical generation method (chemical, electrochemical, sonochemical or photochemical).

2.5.4 Electrochemical Treatment

Electrochemistry is a branch of physical chemistry plays an important role in most areas of science and technology. Furthermore, it is increasingly acknowledged as a significant means for handling environmental and energy problems facing us today and in the near future. Briefly, electrochemistry deals with the charge transfer at the interface between an electrically conductive (or semi-conductive) material and an ionic conductor (e.g. liquids, melts or solid electrolytes) as well as with the reactions within the electrolytes and the resulting equilibrium. Use of electricity to treat water was first proposed in UK in 1889. The first application of electrochemical technique for water purification the electro coagulation of drinking water was first applied on a large scale in the US in 1946 [66 – 67]. Because of the relatively large capital investment and the expensive power supply, electrochemical treatment of water or wastewater technologies did not find wide application worldwide then [68]. However, due to extensive research in US and USSR during the following half century, the process has gained large amount of knowledge. With the ever-increasing stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide [69].

At present, the electrochemical technologies have reached a state that they are not only comparable with other technologies in terms of cost but also potentially more efficient, and for some situations, electrochemical technologies may be the indispensable step in treating wastewaters containing refractory pollutants [70]. Electrochemical technologies offer various treatment processes such as electro oxidation, electro coagulation, electro disinfection, and electro deposition. An extensive research has been done by many researchers in treating various wastewaters by using electrochemical technologies. Electrochemical technique offers several advantages [71] such as

(i) Versatility - direct or indirect oxidations and reductions, phase separations, concentrations or dilutions, biocide functions, ability to deal with many pollutants: gases, liquids and solids, and can be treated from micro liters to millions of liters

(ii) Energy efficiency – electrochemical processes generally have lower temperature. Potentials can be controlled and electrodes and cells can be designed to minimize power losses.

(iii) Amenability to automation - the electrical variables used in electrochemical processes are suited for facilitating data acquisition, process automation and control.

(iv) Environmental compatibility - the main reagent here, the electron, is a 'clean reagent' and there often is no need for adding extra reagents.

(v) Cost effectiveness - the required equipment and operations are generally simple and, if properly designed, are also inexpensive.

Electrochemical waste destruction shows several benefits in terms of costs and safety. The process runs at very high electrochemical efficiency and operates essentially under the same conditions for a wide variety of wastes. Operation at room temperature and atmospheric pressure reduces the possibility of volatilization and the discharge of unreacted waste. The waste treatment can be terminated within seconds by simply cutting off power to the electrodes. The viability of such methods for sterilization, disinfection, deodorization and similar microbiological applications is also considered. Environmental applications of electrochemistry have been the topic of several recent books and reviews [71 – 73]. The electrochemical method for the mineralization of organic pollutants is a relatively new technology and has attracted a great deal of attention recently.

This technology is of interesting for the treatment of dilute wastewater (COD < 5,000 ppm) and it is in competition with the process of chemical oxidation using strong oxidants.

The electrochemical technique has been successfully tested for various industrial effluents: electroplating; oil mill wastewater; heavy metal, nitrite effluent, Phenol compounds, landfill leachate, restaurant wastewater, laundry wastewater, surfactants and Agro-industry wastewater.

A typical electrochemical treatment process consists of electrolytic cell. The electrolytic cell consists of two electrodes; anode and cathode immersed in an electrical conducting solution and are connected together via an electrical circuit. The electrochemical techniques such as electro oxidation, electro coagulation, electro floatation, electro deposition are increasingly tried for environmental applications. In electrochemical process, the electrolyte has significant effect on formation of oxidizing species during the process. For example, if HCl is used as the electrolyte, H^+ moves toward the negatively charged electrode (cathode) in order to accept electrons and get reduced to hydrogen according to the following reaction.

$$H+e \rightarrow 1/2H_2$$

At the same time, Cl- moves toward the positively charged electrode (anode) to discharge electrons and gets oxidized to chlorine as the following:

$Cl \rightarrow Cl_2 + e$

The species H^+ and Cl^- are called the principal charged species, which are responsible for current flow in the solutions.

2.6.4 Electro-coagulation

Electro- coagulation is a process involving chemical and physical phenomena, which uses sacrificial electrodes for generation of coagulants. The generation of metallic cations takes place at the anode, while H_2 production occurs at the cathode [74 – 75]. Electro coagulation technology offers an alternative to conventional coagulation process, where the metal salts or polymers are added to break the stable suspensions of the colloidal particles. In electro coagulation, coagulants are produced in situ within the reactor without direct addition of any chemicals. Coagulants are produced by the electrolytic oxidation of appropriate anode materials, such as mild steel or aluminum, 33 which result in formation of highly charged polymeric metal hydroxyl species. These species neutralize the electrostatic charges on the suspended solids and facilitate agglomeration resulting in separation from the aqueous phase.

This technique removes metals, colloidal particle, and soluble organic pollutants from aqueous media by introducing highly charged polymeric hydroxide species. The treatment prompts the precipitation of certain metals and salts.

The advantage of electrocoagulation is effective removal of smallest colloidal particles with generation of low amount of sludge [76 – 77]. It has been reported that the adsorption on metal hydroxide generated ‘‘in situ’’ by electrocoagulation is more powerful than the metal hydroxides formed chemically in conventional coagulation. When chemical coagulation is used for treating industrial effluent, secondary pollution is caused by chemical substance. Whereas in electrocoagulation, the metal hydroxide is generated “in situ” and the chances of excess coagulants is strictly eliminated [75].

Generally mild steel and aluminum are used as sacrificial anode in electrocoagulation process. When mild steel is used as an anode, it generates iron hydroxide, Fe (OH) n, where n=2 or 3. In addition to the above hydroxyl species, the electro generated ferric ions form monomeric, ferric hydroxo complexes with hydroxide ions and polymeric species, depending on electrolyte pH, i.e., $FeOH^{2+}$; $Fe(OH)_2^+$; $Fe_2(OH)_2^{4+}$; $Fe(OH)_4^-$; $Fe(H_2O)_2^+$; $Fe(H_2O)5OH^{2+}$; $Fe(H_2O)_4(OH)_2^+$; $Fe(H_2O)_8(OH)_2^{4+}$and

$Fe_2(H_2O)_6(OH)_4^{2+}$; which transform into Fe(OH)3 [68,78-79]. These metallic hydroxides have a strong affinity to disperse particles. The charged hydrolyzed hydroxyl can reduce the net surface charge of the colloidal particles that are in suspension due to the reduction of repulsive potential of electrical double layer. As a result of this, the repulsive 34 forces between the colloidal particles decrease, and bring the particles close to such an extent where the Vander Waal's forces predominate and facilitate agglomeration. Hydrolyzed metal species can be adsorbed on the colloids and creates bridges between the particles. In addition to that, the amorphous solid ferric hydroxide flocs that forms at elevated pH, settle down causing sweep flocculation [75].

Electrocoagulation has been successfully applied on various wastewater treatments, and found to be the promising method for solids/liquids separation attempted to find the optimum condition for colour and total COD reduction from the pulp and paper industry effluent by electrocoagulation and reported more than 97% colour and 77% COD removal under optimum conditions.

Attempted to study the influence of electrolysis time, applied charge density, electrolyte pH and supporting electrolyte concentration on electrocoagulation efficiency for the treatment of pulp and paper industry effluent.

The maximum color removal efficiencies were reported as 92 % and 84 % for mild steel and aluminum electrode respectively. The corresponding maximum COD reduction has been recorded as 95 % and 89 %.

Experimented electrocoagulation of pulp and paper industry effluent using aluminum anode, the authors observed more than 60% COD removal and 90% color removal. The other contributors on electrocoagulation for environmental application are [80 – 82].

From the above discussion, it has been clearly proved beyond doubt that electrochemical technique can be an alternative for treatment of organic effluent with the unique features such as complete mineralization, less energy consumption, no generation of solid sludge etc. [71]. The 35 stringent environmental regulations of pollution control board overtake the growing energy and electrode cost and makes the process economically viable soon.

2.7.5 Electro Oxidation

Defined as an electrochemical process which, by way of special, non-sacrificial electrodes we can obtain compounds capable of strongly oxalating the wastewater we are treating. The oxidation of waste water brings about a major reduction in its BOD and its NH_4content. The method consists of carrying out the oxidation reaction at the anode where pollutants are transferred into non-toxic substances, by decomposition into simpler compounds or transferring into oxidation form. It is used mostly for organic substances. Wastewater treatment by this procedure can be: direct or indirect electrochemical oxidation.

2.7.5.1 Indirect electrochemical oxidation

Strong oxidants are produced on anode and then chemical oxidation take place. The most effective type of the indirect electro-oxidation is creation of hydroxyl radicals via Fenton reagent. In Fenton reaction, highly reactive hydroxyl radicals (·OH) are generated

$H_2O \rightarrow OH + H + e$ 2 ads ……………………………… (2.1)

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$ ……………………………… (2.2)

To avoid the disadvantages of traditional Fenton oxidation such as potential risk in transportation of H_2O_2, a loss of reactive activity and sludge production, a modified process called Electro-Fenton method (EF) has been developed. The EF method has the advantage of allowing a better control of hydroxyl radical production; in the EF method, soluble Fe^{3+}can be cathodically reduced to Fe^{2+} which is known as electrochemical catalysis with E0 = 0.77 V/SHE [83]. The efficiency of this process can be increased if the anodic oxidation with BDD (boron deposited diamond) is paired with a classic electro-Fenton process with carbon fiber or oxygen diffusion cathode [84 85]. Reaction rate of oxidation of organics with hydroxyl radical is extremely high, for example, the reaction rate constant of second order can be 109 – 1010 $mol^{-1} \cdot s^{-1}$[86]. The indirect electro-oxidation rate is dependent on the diffusion rate of strong oxidants electroformed into solution which are able to completely convert all organic into water and carbon dioxide [87]. The electrochemical method of depollution presents many important advantages because it does not need auxiliary chemicals; it is applicable on a large range of pollutants and does not need high pressures and temperatures [88].

Further improvement could be achieved by using of UV radiation. UV lights (λ=365 nm) was successfully used to accelerate the mineralization process [89]. This is the photoelectron-Phenton process.

2.7.5.2 Direct electrochemical oxidation

The Direct electro oxidation takes place directly at the anode through to the generation of physically adsorbed "active oxygen" (adsorbed hydroxyl radical, •OH). Direct EO process is also called electrochemical mineralization (EM) of organic contaminants. It is a relatively new technology for wastewater treatment with moderate concentrations of organic pollutants, the chemical oxygen demand (COD) up to 5 g/l.

The main advantage of technology is that it does not consume chemicals, but just electrical energy. EO does not produce secondary pollution and requiring relatively little additional equipment and maintenance.

Electrochemical oxidation is considered a robust technology and easy to use, for that reasons, it has been used for a diversity of wastewater treatment areas. The main advantages of this technology over other conventional treatments are as follows:

- Electron is the main reagent.
- A simple electrochemical cell is required in the process.
- Addition of chemicals is not required.
- The process is carried out at room temperature and atmospheric pressure.

These advantages make it attractive compared to most other wastewater processes. A key element of this technology is anode material. Investigated the anode: - glassy carbon, Ti/RuO_2, Ti / Pt-Ir, fiber carbon, MnO_2, Pt-black carbon, porous carbon felt and stainless steel. But none of the above has sufficient activity and stability.

Therefore, Pt., PbO_2, IrO_2 and SnO_2 were extensively studied anodes [90 83]. They were the most used ones before new development of the conductive diamond films. Currently an ideal material for the anode is boron doped diamond (BDD). Its characteristics are: high reactivity for organic oxidation, high stability and efficient use of electrical energy. Specific energy consumption for this treatment with 100% current efficiency is approximately 22kWh/kgHPK [91 84]. Example of complete (electro) mineralization is a direct electrochemical oxidation of the herbicide 2, 4, 5-Trichlorophenoxyacetic acid, also known as 2, 4, 5-T and Silvex (trade name) [92 85]. The whole process can be represented by the following reaction:

$C_8H_5Cl_3O_3 + 13H_2O \rightarrow 8CO_2 + 31H^+ + 3Cl^- + 28e^-$…………………… (2.3)

Or by COD during electrochemical decomposition, the theoretical reaction of mineralization 2, 4, 5-T can be written as:

$C_8H_5Cl_3O_3 + 7O_2 \rightarrow 8CO_2 + 3HCl + H_2O$ ……………………… (2.4)

Oxidation potential of the anode is directly dependent on the over potential for oxygen separation and adsorption enthalpy of hydroxyl radicals on the anode surface. It follows that for an anode material: the higher the over potential for oxygen, the greater the oxidizing power of the anode material

In electro-oxidation, the pollutants are destroyed by either the direct or indirect oxidation process. In direct anodic oxidation process, the pollutants are first adsorbed on the anode surface and then destroyed by the anodic electron transfer reaction. In indirect oxidation process, strong oxidants such as hypochlorite/chlorine, ozone, and hydrogen peroxide are electrochemically generated. The pollutants are then destroyed in the bulk solution by oxidation reaction of the generated oxidant. All the oxidants are generated in situ and are utilized immediately [71, 93 – 94]. Among the oxidants, generation of hypochlorite is cheaper and most of the effluents have a certain amount of chloride. Though, direct electrolysis of organic compounds at the anode surface is also possible, a major portion of oxidation is mediated by active chloro species when conducting electrochemical oxidation in the presence of chloride using an undivided cell. The application of indirect electrochemical oxidation mediated by chlorine/hypochlorite has been attempted for treating organic effluents by several investigators.

Experimented electrochemical oxidation of textile dye wastewater using RuO_2/Ti anode in batch electrochemical reactor.The authors reported more than 90% COD removal under optimum conditions. The authors later (2007) attempted to reuse the electrochemically treated textile effluent for dyeing application and reported that the electrochemically treated wastewater can be effectively reused for industrial application. Electrochemically treated ink manufacturing process wastewater containing organic, solvents and surfactants using boron doped diamond electrode and reported complete removal of COD .The electrochemical oxidation of phenolic compounds has been reported by several authors [93].

Mohan et al (2006) reported the influence of anode material on electro oxidation process. The authors compared the performance of SnO_2/Ti, 28PbO2/Ti and RuO_2/Ti anodes for degradation of textile effluent and reported better performance of RuO2/Ti than other anodes. Application of noble metals and metal oxides electrodes for treatment of tannery wastewater has been reported by [95 – 97].

The order of efficiency of anodes for tannery effluent was found to be Pt/Ti followed by PbO_2Ti, MnO2/Ti. Used Doehlert matrix to optimize the significant experimental variables such as temperature, pH, current intensity and time for tanning effluents and reported that the current intensity and the electrolysis time were the main influent parameters on the removal ratio of COD, TOC and electrochemical oxidation of trivalent chromium.

Upendra and Sumathi (2008) studied the removal of pentachlorophenol (PCP) as a model AOX compound in pulp bleaching effluent of a bamboo based mill by electrochemical treatment in batch mode and reported that 10 ppm of PCP in water removed almost completely in less than 10 min at a current density of 0.6 A/dm^2 in the presence of 1000 ppm NaCl serving as an electrolyte and source of chloride ions.

Described the electrochemical oxidation using boron-doped diamond electrodes as an efficient alternative in the treatment of bio-refractory effluents Total organic carbon (TOC) removal was reported higher than 80 % under the selected experimental conditions. Investigated the electrochemical removal of 2-chlorophenol and 2, 6-dichlorophenol from aqueous solutions using porous carbon felt anodes and reduced 2-chlorophenol below the prescribed level. The experimental results showed a satisfactory detoxification, consisting of removal of cyclic chlorinated compounds, could be accomplished by means of this electrochemical method. They developed a mathematical model based on the reaction between chlorophenols adsorbed on the carbon fibers of the electrode and hydroxyl radicals produced by anodic oxidation of water has been proposed to interpret the experimental behavior of the system under different operating conditions.

Attempted to remove ammonia present in the tannery effluent through electro oxidation and recorded more than 90% ammonia removal. [96]Studied electro oxidation of tannery effluent and reported more than 90% removal efficiency under optimum conditions. [97] Studied electrochemical method for tannery effluent treatment and reported that the electrochemical method can be an alternative for conventional chemical and biochemical method for tannery effluent treatment.

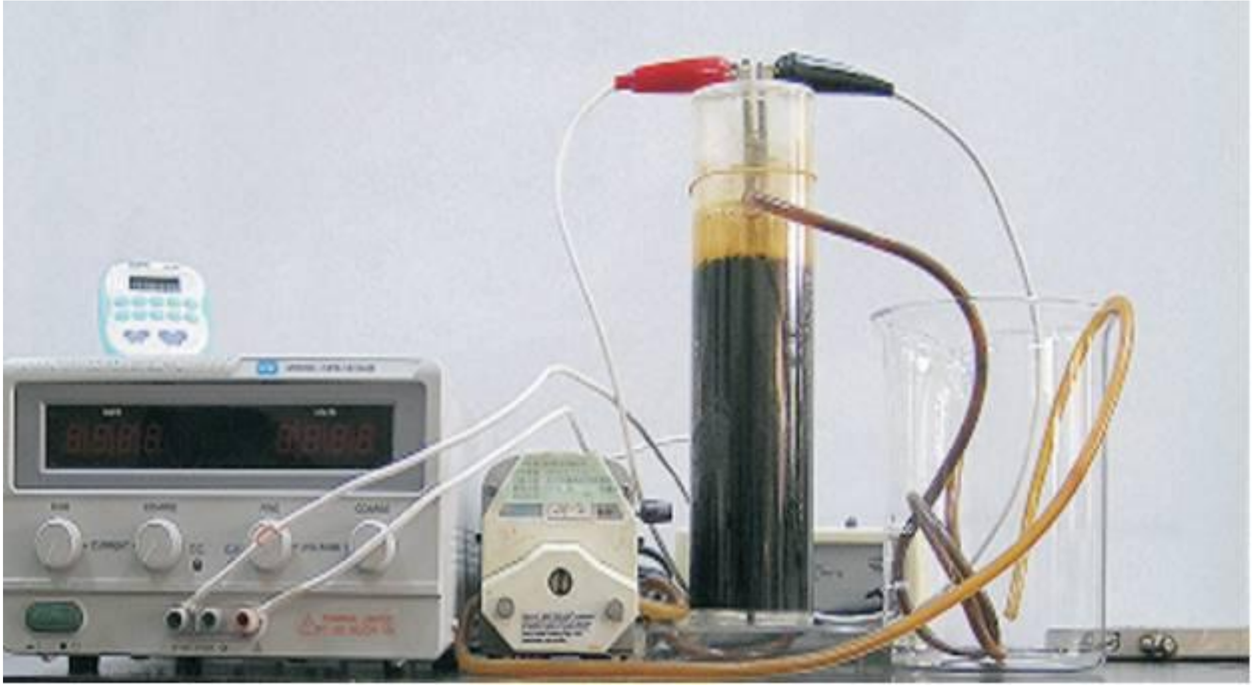

Figure2.2 Electro Oxidation Wastewater Treatment Systems [98]

The treatment and reuse of industrial wastewater has gained greater attention among the industries/researchers due to stringent discharge environmental regulations, diminishing water resources and increased wastewater disposal costs. In Ethiopia, tannery industry is one of the significant contributors to the economy and provides large scale employment opportunity for people of economically weaker society. The transformation of raw skins into commercial products requires high water consumption and the use of several chemicals. Hence, leather processing industry is classified with high organic loads containing priority pollutants such as sulphite, chromium, synthetic tannins (Syntan), biocides etc. The tanning operation in which, organic or inorganic materials become more chemically bound to the available substance and preserve it from deterioration. The characteristics of effluent from tannery industry vary considerably depending upon the plant size, chemicals and type of final product produced. Wastewater from the tanneries contains high biochemical oxygen demand (BOD), chemical oxygen demand (COD), sodium sulphide and suspended solids Some authors attempted both physical and chemical or combination of both for treating leather industrial effluent to reduce organic pollutant and nitrogenous compound present in the leather effluent .The oxidation of organic pollutants with strong oxidants (H etc.) takes place generally at room temperature.

In order to increase the efficiency of mineralization, the oxidation takes place in the presence of catalyst and UV radiation. This technology is interesting for the treatment of dilute wastewater with COD < 5,000 ppm. Although AOP use different reacting systems, but they are characterized by the same chemical feature: production of OH radicals. These radicals are extraordinarily reactive species; they attach the most part of organic molecules with very high rate. OH, radicals are also characterized by a low selectivity of attach which is a useful attribute for an oxidant used in wastewater treatment and to solve pollution problems. The versatility of AOP is also enhanced by the fact that they offer different possible ways for OH radical production thus allowing a better compliance with the specific treatment requirements. AOP are usually classified according to the reaction phase (homogeneous or heterogeneous) or to the OH radical generation method.

2.8 Mechanism of electrochemical oxidation

The mechanism of electro oxidation of organic effluent is a complex phenomenon involving electron transfer reaction with a dissociate chemisorption’s step. In electrochemical oxidation, two types of oxidative mechanism occur at the anode. Oxidation occurs at the electrode surface called direct electrolysis for anodes having high electro catalytic activity. On the other hand, on metal oxide electrode, the oxidation occurs via surface mediator on the anodic surface, where they are generated continuously called indirect electrolysis. In indirect electro oxidation, chloride salts of sodium or potassium are added to the electrolyte for better conductivity and generation of hypochlorite ions. The reactions of anodic oxidation of chloride ions to form chlorine is given as

$$2Cl^- \xrightarrow{k1} Cl_2 + 2e^-$$

$$Cl_2 + H_2O \xrightarrow{k2} H^+ + Cl^- + HOCl$$

$$HOCl \xleftrightarrow{k3} H^+ + OCl^-$$

The liberated chlorine forms hypochlorous acid, further dissociates to give hypochlorite ion. The electrochemical conversion/combustion of organics on a noble oxide coated catalytic anode (MO_x) can be explained as follows.

Adsorbed hydroxide radicals are formed with H_2O discharged at the anode, i.e.

$$MO_x + H_2O \longrightarrow MO_x(^{\bullet}OH) + H^+ + e^-$$

The adsorbed hydroxyl radicals interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hydroxyl radical to the oxide forming the higher oxide MO_{x+1}

$$MO_x(^{\bullet}OH) \longrightarrow MO_{x+1} + H^+ + e^-$$

At the anode surface the “active oxygen” can be present in two states: physiosorbed adsorbed hydroxyl radicals, (•OH) or /and as chemisorbed (oxygen in the lattice, MO x+1). When NaCl is used as supporting electrolyte Cl^- ion reacts with MO (•OH) to form adsorbed OCl^- radicals according to the following.

$$MO_x(^{\bullet}OH) + Cl^- \longrightarrow MO_x(^{\bullet}OCl) + H^+ + 2e^-$$

The MO_x (•OCl) react with Cl^-ion to generate active oxygen (dioxide) and chlorine as given in the following reactions:

$$MO_x(^{\bullet}OCl) + Cl^- \longrightarrow MO_{x+1} + Cl_2 + e^-$$

$$MO_x(^{\bullet}OCl) + Cl^- \longrightarrow MO_x + \tfrac{1}{2}O_2 + Cl_2 + e^-$$

The generated hypochlorite ions act as main oxidizing agent in the pollutant degradation. The organics present in the effluent reacts with $OCl^-$to get converted in to CO_2 and water, i.e.

$$\text{Organics} + OCl^- \longrightarrow CO_2 + H_2O + Cl^-$$

The electro oxidation reaction rate of organic pollutants depends on the catalytic activity of the anode, the diffusion rate of the organic compounds in the active points of anode and applied current density. During the electrochemical generation of hypochlorite ion, the following side reactions may occur.

Chlorate may be formed either chemically or electrochemically when hypochlorite ions reached saturated level, i.e.

$$2HClO + ClO^- \longrightarrow ClO_3 + 2H^+ + 2Cl^-$$

And

$$6OCl^- + 3H_2O \longrightarrow 2ClO_3 + 6H^+ + 4Cl^- + \frac{1}{2}O_2 + 6e^-$$

The side reactions should be controlled in order to get better oxidation efficiency. The pseudo steady state theory can be applied to each of the intermediate's products (HOCl and OCl) taking part in the bulk solution

Chapter Three

3. Materials and Methods

This chapter presents the raw material, chemical, and reagent required for this research and the experimental procedures followed, the instruments used for treat soaking liquor, characterized and analysis, an illustrate and depicting of the experimental setup.

3.1 Materials

3.1.1 Raw materials and Reagent

Wet-salted hide soaking liquor is wastewater obtained from beam house operation of batu tannery and it is used as a model pollutant for the series of batch electro-chemical oxidation experiment. This wastewater liquor has highly contained organic and inorganic pollutants in the ranges of TDS and salt concentration of 7315- 4120 mg/l and 17000-13500 mg/l respectively and it influenced the wastewater treatment on the parameter of BOD, COD, and TDS.

Analytical grade reagents (potassium dichromate used to standardize ferrous ammonium sulfate); mercuric sulphate used to remove chloride interference. $HgSO_4$, standard ferrous ammonium sulfate, ferrion as indicator, this indicator is used to indicate change in oxidation-reduction potential of the solution and indicates the condition when all dichromate has been reduced by ferrous ion. Sulfuric acid (sp.gr. 1.84) used to dissolve HgSO4, calcium carbonate, PO_4 starch solution as indicator, sodium thiosulphate, H_2O_2, K_2CrO_4, silver nitrate is used as a catalyst for COD measurement, distilled water, chemicals for characterization and determination of wastewater characteristic. The parameter such as BOD, COD, TDS, and chloride content were used a main parameter.

3.1.2 Equipment

The equipment and tools used throughout the experiments to achieve the objective of the study are: 300 ml BOD bottles with ground glass stoppers, BOD incubator (20^oC +/- 1^oC), pipets and DO meter, Burettes and pipettes 500ml refluxing flask for COD analysis. The equipment used to conduct the analysis of TDS includes: glass fiber filters, membrane filter funnel or Gooch crucible, filter flask, vacuum source, drying oven, desiccator and an analytical balance, refrigerator (For keeping raw waste water until goes the treatment), and main equipment of this projects is Electro oxidation machine (for treatment of the wastewater of organic pollutant). All of these equipment's were obtained from leather technology and physical laboratory of LIDI.

Figure 3.1 Setup of the lab-scale electro oxidative reactor fig 3.2 COD Measurement

Fig 3.3 BOD incubator

fig 3.4 TDS Measurement

3.2 Methods

3.2.1 Sample Collection and Preparations

Enough amounts (20 liter) of tannery wastewater samples (soaking liquor) were collected from Batu and leather industry development institute. The effluent was collected in polythene containers of 2 liters capacity from each batch and was brought to the laboratory with due care and was stored at 20^{o}C for further analysis. Chemicals used for the analysis of spent liquor were analytical grade reagents. The leather industry wastewater was filtered through sand filter paper (pore size 11μm) to separate the solid particles present in the wastewater. After filtration, the physical and chemical characteristics of tannery soaking effluents parameters pH, color, COD, BOD, total dissolved solids (TDS), and total suspended solids (TSS), chlorides were analyzed as per standard procedures [97]. The samples were filtered before subjecting to the electro-oxidation process and characterization.

3.2.2 Experimental set-up

The electro-oxidation process has been carried out in a cylindrical cell of effective capacity of 2 liters. A Cylindrical graphite electrode with a diameter of 2.54 cm and a length of 13 cm was shown in both the electrodes were cylindrical and placed parallel as shown in figure 3.1.

Surface area of the electrodes was 427.84 cm^2. The electric power supply was provided by the laboratory direct current power source equipped with current-voltage monitoring [93].

All the batch electrochemical oxidation experiments were performed in this experimental set up

For all the experiments, the current density of 0.012A/cm^2 was maintained. The salt concentration was varied from 5 to 10 g/l with and increment of 5,000 mg^{-1}/ L. The electro-oxidation process time was 2 hours and the samples collected for every 30 min intervals were subjected to BOD, COD, and TDS. The free chlorine was analyzed for varying salt concentrations.

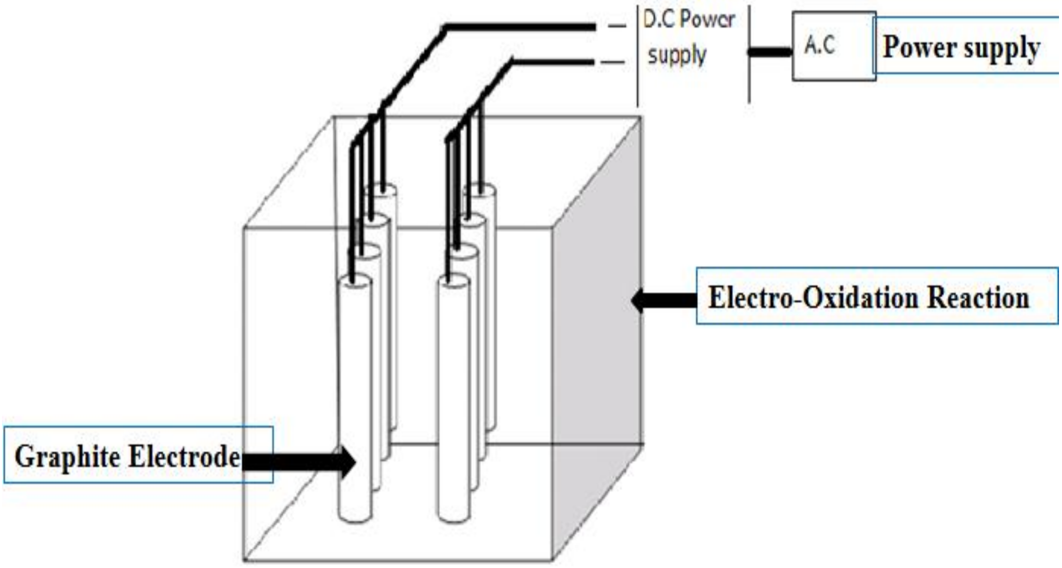

Figure 3.5 Experimental Setup of the lab-scale electro oxidative reactor. [93]

3.2.3 Analysis and Characterization of Wastewater

Determination of pH:

The pH of wastewater was determined by measurement of the electro motive force (emf) of a cell comprising of an indicator electrode (an electrode responsive to hydrogen ions such as glass electrode) immersed in the test solution and a reference electrode (usually a calomel electrode) model number HI 710005 and +/-0.02 pH accuracy . Contact is achieved by means of a liquid junction, which forms a part of the reference electrode.

Determination of Chemical Oxygen Demand (COD):

The chemical oxygen demand was determined by open reflux method. For samples with a COD of >900 mg O2/L, use smaller portion diluted to 50.00 mL. Add 1 g HgSO4, several glass beads, and very slowly add5.0 mL sulfuric acid reagent, with mixing to dissolve HgSO4. Cool while mixing to avoid possible loss of volatile materials. Add 25.00 mL 0.04167M $K_2Cr_2O_7$ solution and mix. Attach flask to condenser and turn on cooling water. Add remaining sulfuric acid reagent (70 mL) through open end of condenser. Continue swirling and mixing while adding sulfuric acid reagent.

Cover open end of condenser with a small beaker to prevent foreign material from entering refluxing mixture and reflux for 2 h. Cool and wash down condenser with distilled water. Disconnect reflux condenser and dilute mixture to about twice its volume with distilled water. Cool to room temperature and titrate excess $K2Cr_2O_7$ with FAS, using 0.10 to 0.15 mL (2 to 3 drops) ferroin indicator. Although the quantity of ferroin indicator is not critical, use the same Volume for all titrations. Take as the end point of the titration the first sharp color change from Blue-green to reddish brown that persists for 1 min or longer. Duplicate determinations should agree within 5% of their average. The blue-green may reappear. In the same manner, reflux and titrate a blank containing the reagents and a volume of distilled water equal to that of sample [97].

COD (mg/l) = (blank value-titrated value) ×N of FAS×8000/ volume of sample …….3.1

Determination of biochemical oxygen demand (BOD):

Biochemical oxygen demand (BOD) of an effluent is the milligram of oxygen required to biologically stabilize one liter of that effluent (by bio-degradation of organic compounds with the help of micro-organisms) in 5 days at 4^{o}C.If the BOD value of an effluent is high, then that effluent contains too much of bio-degradable organic compounds and so will pollute the receiving water highly. It was determined as follows:

Take 5 liters of distilled water, aerated for 3.5 hours, added nutrients 1 ml nutrient for 1-liter aerated distilled water (FeCl, $CaCl_2$, PO_4, $MgSO_4$, domestic water), aeration for 30 minutes.

BOD bottle (300 ml), add sample, fill the bottle with aerated water, put the lid (avoid air bubbles), keeping BOD incubator at 20oC for 5 days, after 5 days take the bottle and add 2 ml $MnSO_4$, 2 ml alkalized iodide and 2 ml conc. H_2SO_4. Shake the bottle well (yellow colour) take 200 ml sample add starch solution as indicator (purple colour) titrated with 0.025 N sodium thiosulphate end point colour change from purple to colorless.

In blank filled the bottle with aerated water without the sample and follow the procedure [97].

BOD_5= (blank value- titrated value) ×300/volume of sample …….3.2

Determination of total dissolved solid:

Dry weight of empty dish or crucible (initial weight) take sample and filter with What man No.1, add 50 ml filtrate sample, keep it in water bath until dry, keep it in oven (103 to 105^{o}C) for at least 1 hour, desiccator, take final weight of dish [97].

Total dissolved solid (mg/l) = (final weight-initial weight) ×1000×1000 / volume of sample...3.3

Stir sample with a magnetic stirrer and pipet a measured volume onto a glass-fiber filter with applied vacuum. Wash with three successive 10-mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete. Transfer total filtrate (with washings) to a weighed evaporating dish and evaporate to dryness on a steam bath or in a drying oven. If necessary, add successive portions to the same dish after evaporation. Dry evaporated sample for at least 1 h in an oven at 180 ± 2°C, cool in a desiccator to balance temperature, and weigh.

Repeat drying cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less [97].

$mg\ total\ dissolved\ solid/L = (A - B)\ x\ 1000)/\ (sample\ volume,\ mL)$ …………….3.4

Fig 3.6 Wastewater sample in the oven for TD and TDS analysis

Determination of chloride:

Use a 100-mL sample or a suitable portion diluted to 100 mL. If the sample is highly colored, add 3 mL Al (OH) suspension, mix, let settle, and filter.

If sulfide, sulfite, or thiosulfate is present, add 1 mL $H2O2$ and stir for 1 min. directly titrate samples in the pH range 7 to 10. Adjust sample pH to 7 to 10 with $H2SO4$ or NaOH if it is not in this range. For adjustment, preferably use a pH meter with a non-chloride-type reference electrode. (If only a chloride-type electrode is available, determine amount of acid or alkali needed for adjustment and discard this sample portion. Treat a separate portion with required acid or alkali and continue analysis.) Add 1.0 mL $K2CrO4$ indicator solution. Titrate with standard $AgNO3$ titrant to a pinkish yellow end point. Be consistent in end-point recognition.

Standardize $AgNO3$ (0.01N) titrant and establish reagent blank value by the titration method outlined above. A blank of 0.2 to 0.3 mL is usual. [97].

Chloride (mg/l) = (A-B) ×N. of silver nitrate×35.45×1000/ volume of sample …….3.5

A = ml titration for sample

B = ml titration for blank

N = normality of $AgNO_3$

3.2.3 Design of the Experiment

The experimental runs were conduct randomly and suitable analysis technique has been carried out by Design -Expert version 7.0 software. In addition, central composite design to evaluate the effects of the process variables; pH (7 – 9), electro-oxidation time with interval of 30' (30min,60min, 90 min and 120 min) and salt concentration (13.5g/l, 14 g/l and 15 g/l) pH, electro-oxidation time and salt concentration respectively were used center point. A 24 full factorial experimental design with 20 experiments were employed, which includes 8 trails for factorial design, 6 trails for axial points and 6 trails for replication of the central points to estimate error based on the pattern generated through software. The response variable was soaking wastewater before and after treatment of EO. This design of the experiment helps us to optimize by varying the PH and salt concentration for process parameters wastewater of COD, BOD and TDS. Significance of the result was set from analysis of variance (ANOVA) under the response of COD, BOD and TDS.

Table 3.1 Experimental factors and levels

name	Factor	Unit	Low level	Center	High level
pH	A	-	7	8	9
Salt concentration	B	mg/L	13.5	14	15
EO-Time	C	Minute	30	60 – 90	120

Table C.1 The experimental design and predicted responses for wastewater of EO

Run	Factor 1: pH (A)	Factor 2: Time(min.) (B)	Factor 3: Salt concentration (g/l) (C)	Response 1 COD (%)	Response 2 BOD (%)	Response 3 TDS (%)
1	9	30	15	65.12	42.96	15.45
2	7	60	14	34.11	35.58	0.22
3	9	90	13.5	70.87	56.26	0.97
4	7	30	15	66.11	42.95	14.45
5	7	30	13.5	46.4	13.97	0.93
6	9	120	15	84.4	84.06	10.46
7	9	120	14	73.6	73.59	9.51
8	9	60	14	36.49	31.52	4.03
9	9	90	14	75.02	64.88	0.36
10	7	120	13.5	58.7	58.70	7.12
11	7	90	15	47.35	46.20	3.93
12	9	60	15	69.88	53.33	0.27
13	7	90	14	74.5	58.60	12.53
14	7	120	15	83.56	84.06	10.43
15	7	60	15	64.25	47.41	8.68
16	9	30	13.5	47	14.03	0.83
17	7	60	13.5	67.12	46.29	15.28
18	9	30	14	62.69	38.88	-1.24
19	9	120	13.5	59.31	58.83	6.21
20	7	90	13.5	68.83	52.72	12.51
21	7	30	14	63.23	38.88	8.23
22	9	60	13.5	68.32	46.29	15.45
23	9	90	15	47.35	45.61	0.56
24	7	120	14	73	73.22	9.88

To analysis soaking wastewater physico- chemical properties, pollution parameters such as Color, chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solid (TDS) and chlorides (Cl^-) were analyzed by following the standard procedure [97].

All the batch electrochemical oxidation experiments were performed in this experimental setup.

The third treat and optimize the raw soak wastewater organic pollutant using electro-oxidation the effects of pH, salt concentration and electrolysis time.

The finally, characterize and evaluate the treated wastewater according to the waste water treatment standard. Characterization of the raw and treated effluent has shown in fig. 3.2.

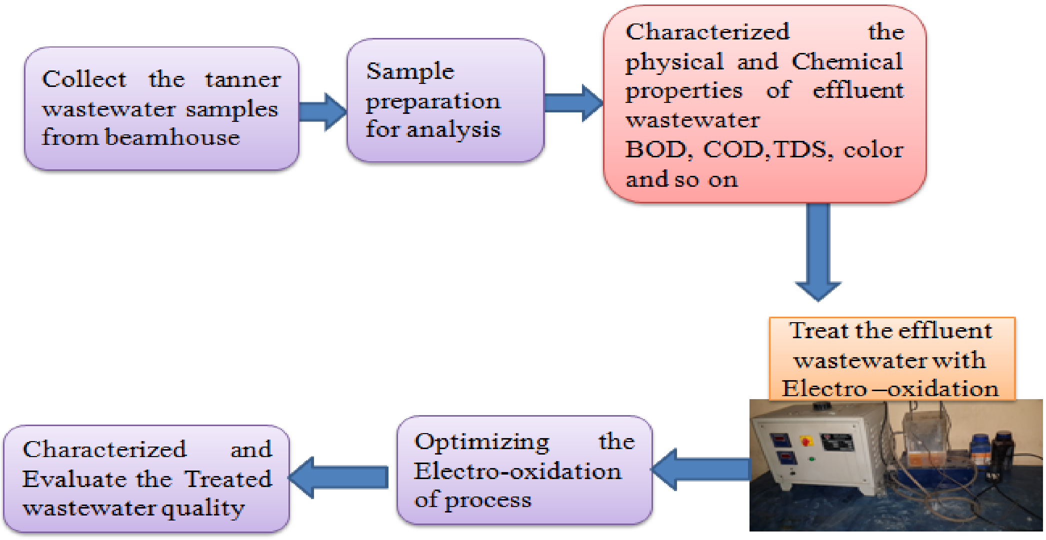

Figure 3.7 Characterization of the raw and treated effluent

3.3 Statistical Analysis

The result of the electro-oxidation of soaking liquor analyses was the results of all physical testing were statistically evaluates using ANOVA. All experiments were carried out in triplicates. All data were stated as mean standard deviation Analysis of variance (ANOVA) at a 5% level of significance was used to compare the electro-oxidation of soaking liquor with the factors affecting the process. The result was analyzed using statistical software Design Expert version 7.

Chapter Four

4. Results and Discussion

4.1 Characteristics of Raw Soaking Wastewater

The physico-chemical characterization of the soaking wastewater (color, pH, BOD, COD, and TDS & Cl^-) has been determined for different batch process and tabulated in Table 4.1. Physicochemical parameters have following the standard methods for analysis of water and wastewater

Table 4.1Raw soaking liquor Physico-chemical quality

Parameter	**Load in Soaking waste water(mg/l)**			**Average**	**Discharged Limit according Ethiopia Standard**
	Sample 1	**Sample 2**	**Sample 3**		
Color	Intense brown	Intense brown	Intense brown		-
PH	8.37	8.44	7.9		6 – 9
BOD (mg/l)	661	1082	882	1378	>90% Removal or 200
COD (mg/l)	2056	3330	2776	2720	500
TDS (mg/l)	6510	4120	7315	5981.7	
Chloride (mg/l)	15800	13500	17000	15,433	1000

Except pH & color all values are expressed in mg/l

As show the above table the value of each wastewater parameter is greater than the Ethiopian standard limit. So, we need further treatment of the soaking liquor to reduce the wastes parameter under the Ethiopia standard by using of advanced organic treatment (Electro chemical oxidation).

4.1.1. Characteristics of Treated Soaking Wastewater

The concentration of 13,500 mg/L, 3.5 % (w/v) of soak liquors means, 13,500 mg of dried sodium chloride dissolved in 1000 mL of soak liquors. The result of BOD, COD & TDS parameters has shown at table 4.2

4.2.1 Effect of salt concentration

The concentration of sodium chloride in soak water liquor treatment was varied from 13.5 – 15 g/L with an increasing order of 5-10 g/L; the pH varied from 6-9 and current density is constants at 0.012A/cm^2 respectively. COD and BOD reduction rate was found to be directly proportional to the salt concentration as shown in table 4.3a & b. Reduction of COD and BOD was increased with increase in salt concentration. However, the increase in the reduction of COD with respect to increasing the salt concentration was insignificant. Highest reduction in COD and BOD were observed as 84.4 % and 84.06 % at salt concentration of 15 g/L.

Table 4.2 Characteristics of soaking wastewater after treatment through electro-oxidation at salt concentration of 13,500 mg L^{-1}

Parameter	**Time @ 0 min**	**Time @ 30 min**	**Time @ 60 min**	**Time @ 90 min**	**Time @ 120 min**
pH	8.37	7.43	6.83	7.48	7.55
COD	2056	1102	767	717	676
% removal of COD	0	46.40	62.69	65.12	67.12
BOD	661	580	404	377	355
% removal of BOD	0	13.97	38.88	42.96	46.29
TDS	6510	6450	6530	5505	5515
% removal of TDS	0	0.22	0.27	0.97	0.36

The values of COD, BOD and TDS efficiency were about 75.02 % and 64.88 % and 0.36 %,(a) respectively and 71.5%, 56.6 and 12.53(b) for the other batch soaking liquor when we see the result of batch (a) and (b) the reduction of COD is almost the same and the result of TDS is different for each experiment with a maximum treatment period of 120 min. The result observed at Table 4.3.

At the salt concentration 14,000 mg L^{-1}.The electro-oxidation was carried out at different time, temperature and pH and the effect of those factors obtained are tabulated in Table 4.3.

The concentration of 14,000 mg/L, 4 % (w/v) of soak liquors means, 14,000 mg of dried sodium chloride dissolved in 1000 mL of soak liquors. The result of BOD, COD & TDS parameters has shown at table 4.3

Table 4.3 Characteristics of soaking wastewater after treatment through electro-oxidation at salt concentration of 14,000 mg L^{-1}

Parameter	**Time @ 0 min**	**Time @ 30 min**	**Time @ 60 min**	**Time @ 90 min**	**Time @ 120 min**
pH	8.44	7.81	8.02	8.07	8.11
COD	3330	2194	1003	970	832
% removal of COD	0	34.11	69.88	70.87	75.02
BOD	1082	697	505	476	380
% removal of BOD	0	35.58	53.33	56.00	64.88
TDS	4120	4111	4100	4080	4105
% removal of TDS	0	3.93	7.12	9.51	10.46

(a)

Parameter	**Time @ 0 min**	**Time @ 30 min**	**Time @ 60 min**	**Time @ 90 min**	**Time @ 120 min**
pH	7.9	6.38	6.01	6.07	6.71
COD	2776	1763	1270	1004	790
% removal of COD	0	36.49	54.25	63.83	71.5
BOD	882	604	552	417	365
% removal of BOD	0	31.52	37.41	52.72	56.6
TDS	7315	7020	6680	6400	6399
% removal of TDS	0	4.03	8.68	12.51	12.53

(b)

The values of COD, BOD and TDS efficiency were about 84.4 % and 84.06 % and 10.46 %, respectively for each experiment with a maximum treatment period of 120 min the result has been shown at Table 4.4.at the salt concentration 15,000 mg L^{-1}.

The electro-oxidation was carried out at different factors such as time, temperature and pH and the effect of those factors obtained are tabulated in Table 4.4

Table 4.4 Characteristics of soaking wastewater after treatment through electro-oxidation at salt concentration of 15,000 mg L^{-1}

Parameter	**Time @ 0 min**	**Time @ 30 min**	**Time @ 60 min**	**Time @ 90min**	**Time @ 120 min**
pH	8.44	7.81	7.54	6.75	7.11
COD	4896	2634	2022	1293	764
% removal of COD	0	46.2	58.7	73.6	84.4
BOD	1632	878	674	431	260
% removal of BOD	0	46.20	58.70	73.59	84.06
TDS	7515	7220	6980	6800	6729
% removal of TDS	0	0.93	-1.24	15.45	15.28

The value has gotten from the concentration of salt 15,000mg/l of the soaked liquor with electro-oxidation treatment the value of BOD and COD after 120min is 260mg/l and 764 mg/l respectively. So, the result achieves the Ethiopian standard limit, 200 and 500 respectively.

The reduction of soaking wastewater parameter before and after electro oxidation treatment shown at figure 4.1

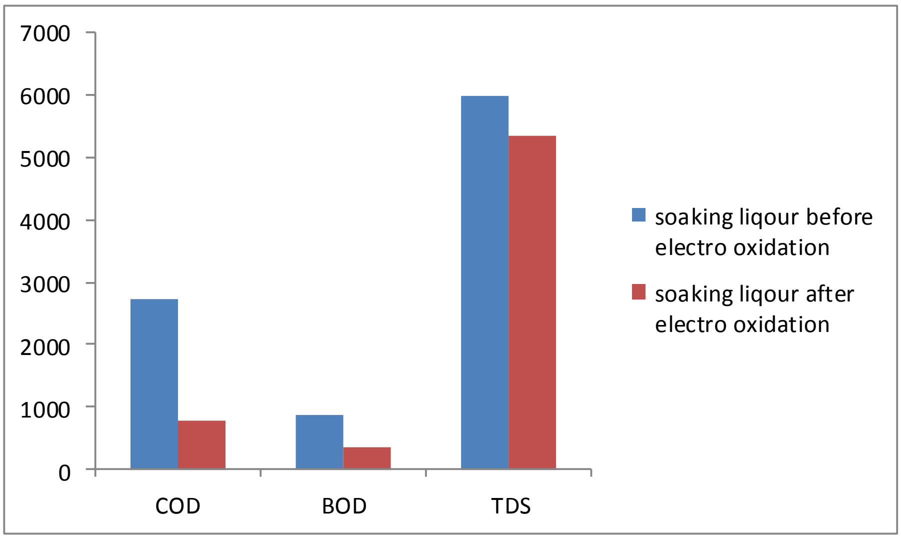

Figure 4.1 the parameter of the pollution of waste water before and after treated

4.1.2. Effect of pH

The effect of pH on the electro-oxidation of Soak wastewater was investigated for a wide range of pH varied from 6 to 9 and NaCl concentration of 0.012A/cm^2 /cm2 and 15 g/L respectively. The rate of COD reduction, BOD reduction and TDS reduction with respect to time is shown in table 4.4. COD was reduced by 73.6 % and 84.4 %, BOD was reduced by 73.59 % and 84.06 % at pH 6.75 and 7.11 respectively. But increase in pH resulted in the increase in the degree of reduction of COD. Soak water before and after treatment was characterized and reused. The removal of organic load was assessed by estimating BOD and COD.

Effects of pH on BOD and COD the soaked wastewater during electro oxidation treatment the result had shown at fig.4.2.

Electro-oxidation of tannery soak water at pH 7 with process time was shown in Table 4.5

Table 4.5 Characteristics of soaking wastewater after treatment through electro-oxidation at pH of 7

Parameter	**Time @ 0 min**	**Time @ 30 min**	**Time @ 60 min**	**Time @ 90 min**	**Time @ 120 min**
pH	7.0	6.89	7.63	7.84	7.89
COD	4896	2743	2000	1300	699
% removal of COD	0	44.58	59.15	73.44	83.72
BOD	1632	900	670	430	259
% removal of BOD	0	44.85	58.94	73.65	84.12
TDS	7515	7200	6970	6801	6730
% removal of TDS	0	4.19	7.25	9.50	10.45

Table 4.6 Characteristics of soaking wastewater after treatment through electro-oxidation at pH of 8

Parameter	**Time @ 0 min**	**Time @ 30 min**	**Time @ 60 min**	**Time @ 90 min**	**Time @ 120 min**
pH	8.0	7.92	8.52	8.76	8.81
COD	4896	2190	1090	776	692
% removal of COD		55.26	77.73	84.15	85.86
BOD	1632	834	600	550	420
% removal of BOD		48.89	63.23	66.29	74.26
TDS	7515	7190	6813	6800	6773
% removal of TDS	0	4.32	9.34	9.51	9.87

Table 4.7 Characteristics of soaking wastewater after treatment through electro-oxidation at PH of 9.

Parameter	**Time @ 0 min**	**Time @ 30 min**	**Time @ 60 min**	**Time @ 90 min**	**Time @ 120 min**
pH	9.0	9.4	9.54	9.78	8.81
COD	4896	2611	2000	1280	760
% removal of COD	0	46.67	59.15	73.85	84.47
BOD	1632	872	667	425	256
% removal of BOD		46.56	59.12	73.95	84.31
TDS	7515	7219	6978	6790	6723
% removal of TDS	0	3.94	7.15	9.65	10.54

The process standardization of electro-oxidation of tannery soak wastewater was carried out by studying the effects of pH, current density, salt concentration and electrolysis time. For these studies, the soak tannery wastewater was used. For first set of experiments, pH had been varied from 7 to 9 with an increment of 1. Current density and NaCl concentration were kept constant at 0.012A/cm^2 and 15 g/L of NaCl. COD was reduced by 83.72, 85.86, and 84.47% and at pH 7, 8 and 9 respectively.

At pH 7 the result value of COD has shown 83.72% reduction but in the case of pH at 8 the COD reduction 85.86% and at pH 9 the COD reduction is 84.47%, this result has shown when the pH increases the COD reduction value increasing but at 9 pH some value reduction obtained. So, the optimized pH for reduction of the COD of soaking liquor with EO treatment is around 8. In the case of BOD and TDS at pH 7 BOD and TDS reduction is higher than at pH 8 and again rise at pH 9. The pH is directly proportional to the COD reduction and inversely proportional to BOD reduction

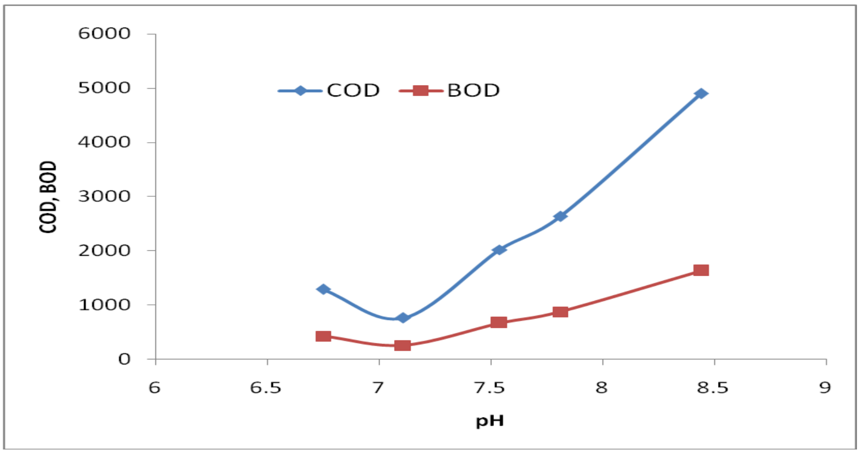

Figure 4.2 Effect of pH on COD, BOD During electro oxidation: Salt concentration = 14000 mg/L

4.2 DISCUSSION

The findings of this study are in accordance with those of Sundarapandiyan et al (2) which showed that an increase in pH from 5 to 11 causes a COD decreases from 89% to 57%. According to Equations 1-5, the reason for this is that in acidosis state, hypochlorite ions, CLO- , remains unstable and in combination with hydrogen ion tends to form HCLO. The hypochlorite which is formed in an alkaline state accounts for the most important factor inorganic matter oxidation. However, Yan et al (18) reported a higher removal of COD in acidic conditions using the Fenton process as it is more efficient in acidic conditions. results for the effects of reaction time on COD removal at 15g/L salt concentration, pH=8.4, and 0.012A/cm^2 current density showed that reaction time had a significant effect on this process The mean COD removal of was 46.2% 30 minutes reaction time and 84.4 at 120 minutes reaction time (Table 4.4). Increase in reaction time, COD removal also increases. Results for the effects of salt concentration on COD removal at 2 hour reaction time, pH=9, and 0.012A/cm^2 current density showed that salt concentration had a significant effect on the process.

In comparing different concentration of NaCl, it is observed that 15g/L salt concentration is significantly different from 13.5g/l and 14g/l NaCl.

Determination of pH

The extreme pH of wastewater is generally not acceptable, as lower pH cause problems to the survival of aquatic life. It also interferes with the optimum operation of wastewater treatment facilities. Water with high or low pH is not suitable for irrigation. At low pH, most of the metals become soluble in water and therefore could be hazardous in the environment. At high pH, most of the metals become insoluble and accumulate in the sludge and sediments. The toxicity of heavy metals also gets enhanced at a particular ph. The result of this study shows that the increase in COD reduction from pH 7.0 to pH 9.0 was found to be relatively significant. Therefore neutral and alkaline conditions are favorable for pollution reduction. The rate of COD reduction with respect to PH is shown in Fig. 4.3.

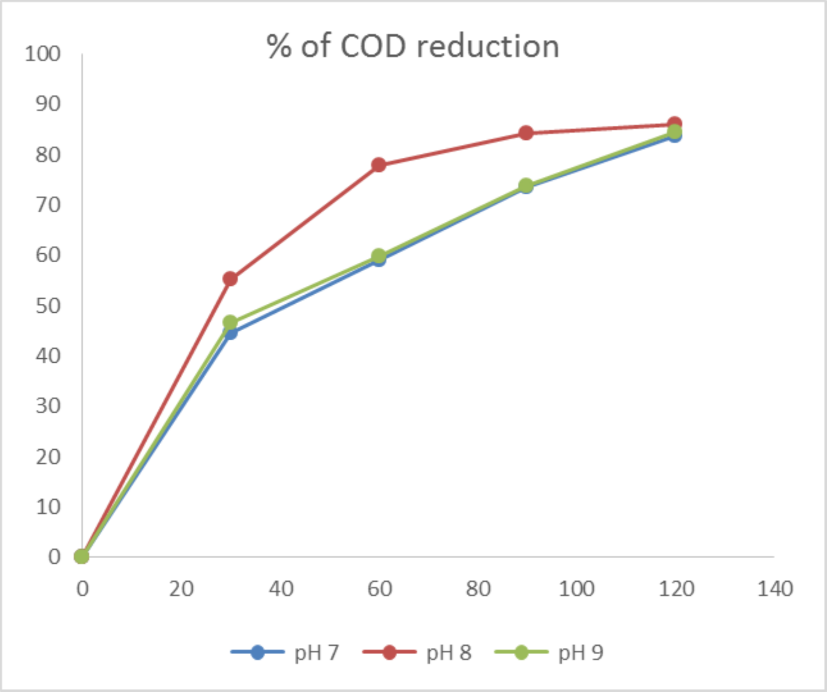

Figure 4.3 Effect of pH with electro-oxidation time on COD reduction with the salt concentration 15g of NaCl/L**.**

i. Determination of Biochemical Oxygen demand (BOD)

BOD is a measure of the content of organic substances in the wastewater which are biologically degradable with the consumption of oxygen. The 5-day Biochemical oxygen demand (BOD5) usually indicated. This is the amount of oxygen in milligrams per liter (O_2) (mg/l) that consumed by microorganisms in 5 days at 20^{o}C for the oxidation of the biologically degradable substances contained in the water. The results of the present study revealed that the BOD level from different batch tanning processes at the soaking process was given in Fig. 4.5 indicating a high organic load surpassed the legal limit set by EPA (200 mg/l). The presence of organic matter will promote anaerobic action leading to the accumulation of toxic compounds in the water bodies.

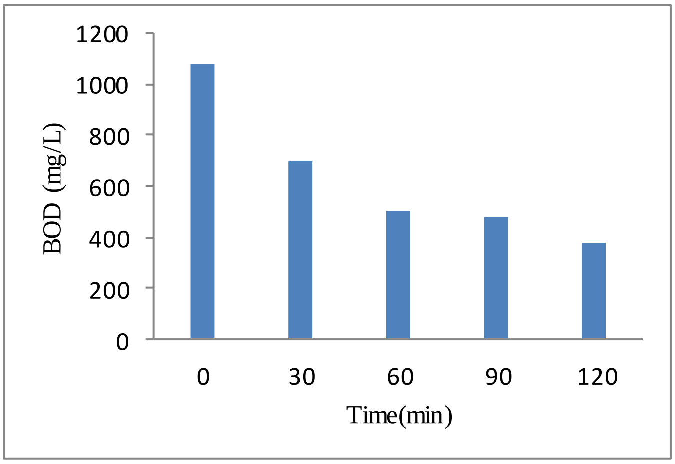

Figure4.5 Biological oxygen demand at different time intervals

Determination of Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is a quantity of oxygen expressed in milligram consumed by the oxidizable matter contained in one liter of the sample. The test is performed by vigorous oxidation with chemicals and back-titrating the chemical consumed for oxidation. COD is a system of measuring the content of organic impurities with oxidizing agents. The results of the present study revealed that the COD level from different batch tanning processes at soaking, the result was given in Fig. 4.6 exceeds the permissible COD level EPA (500mg/l). This indicates that the effluent is unsuitable for the existence of the aquatic organisms, due to the reduction in the dissolved content.

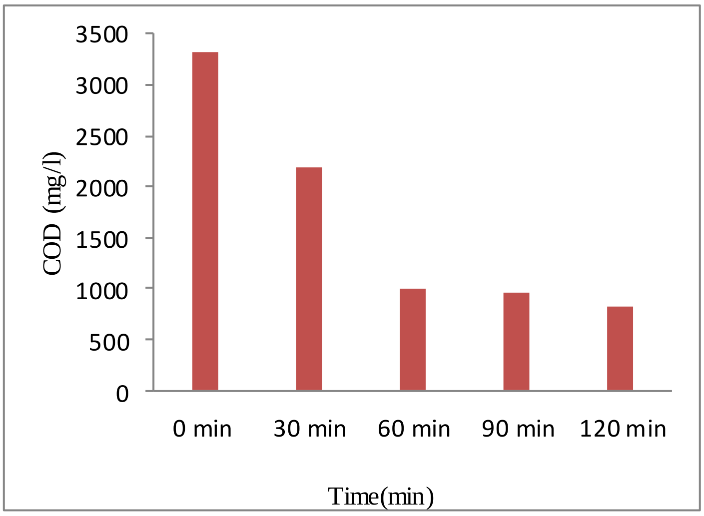

Figure 4.6 Chemical oxygen demands at different time intervals.

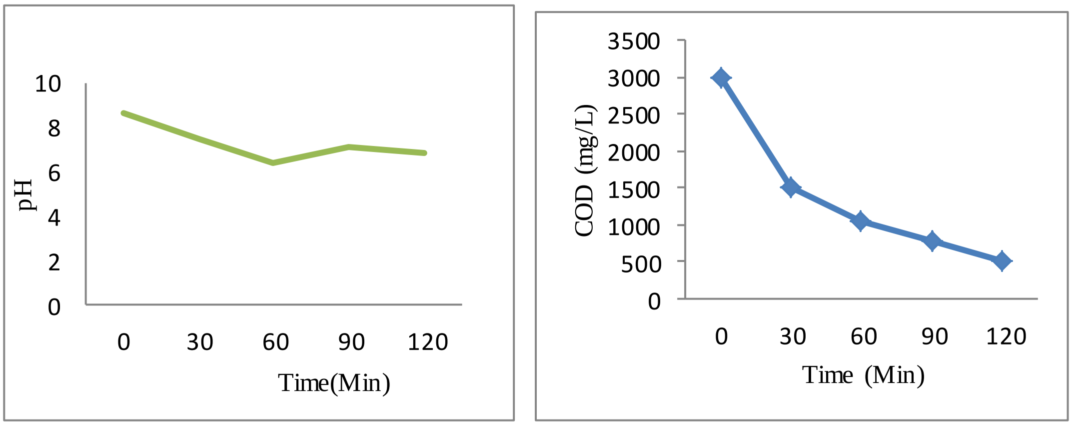

Figure 4.7 the profile of variation (a) pH and (b) COD, with time during Electro – oxidation at temperature 25^{O}C

After a specific period of time, even though the oxidation mechanism removes the organic matter continuously, the ratio of BOD and COD easily degradable to very slowly. In electro-oxidation treatment, the initial reaction on slowly biodegradable long chain molecules, results in an increase the soaked wastewater organic pollutant degradation. The characterization of the soak liquor showed that this effluent is biodegradable, though not easily and highly variable depending on the origin and the nature of the hides.

ii. Determination of Chloride

The results of the present study revealed that the chloride level from soaking is 15,433 mg/ l (Table 4.1) and the levels exceed the permissible chloride level of 1000 mg/L of effluent discharge into inland surface waters. High levels of chlorides in the tannery effluent could be attributed to the soaking processed. The chloride content in the water sample gives an idea of the salinity of the water sample.

Chapter Five

5. Conclusion and Recommendation

5.1 Conclusion

In this study, soaking saline tannery wastewater was used as a model pollutant. Soak wastewater before and after treatment was characterized for its physicochemical properties. The soaked liquor was treated with electro oxidation at varies factor such as pH, contact time and concentration of salt. The characterization of the soak liquor showed that soaked liquor can be effectively with electro-chemical oxidation technique , though not easily and highly variable depending on the origin and the nature of the hides. After a specific period of time, even though the oxidation mechanism removes the organic matter reasonably, the ratio of BOD and COD degradation rate is very slowly. At the studied condition, colorless removal of 95%, COD, BOD and TDS removal of 85.86 %, 84.31 %, and 12.51 % of was achieved at PH of 8 and 9 respectively. Highest reduction in COD and BOD were observed as 84.4 % and 84.06 % at salt concentration of 15 g/L, respectively. The electro-oxidation for the treatment of soak liquor was attempted and the results displayed more than 75% of organic load reduction within 30 – 120 minutes,

In general, it can be concluded that the electro oxidation process can be considered as an attractive, alternative and can be successfully applied for soaking wastewater treatment.

5.2 Recommendation

From the study the treated soak liquor is surpassed the legal limit set by EPA therefore in the future we recommend,

- Reuse of the treated soak water for washing liming wastewater, pickle stage and leather processing soaking itself and also use for agriculture purpose (salt loving plants). Such initiatives would reduce on the water consumption.
- Perform the treated solution to be evaporated to dryness to get NaCl salt for hide/skin preservation

- In this study, show as only the effect of pH, concentration and contact time. However, other parameters are not included so, it needs further study to increase the efficiency electro oxidation.
- Estimate the cost of the treatment process and provide a cost benefit ratio analysis.

Reference

1. United Nation Industrial Development Organization (UNIDO) (2015) Report: Waste generated in the leather products industry. Zlin, Czech Republic.
2. Kara bay S (2008) Waste management in leather industry. DokuzEylul University, Turkey.
3. Bosnic M, Buljan J, Daniels RP (2000) Pollutants in tannery effluents definitions and environmental impact limits for discharge into water bodies and sewer. UNIDO; Regional Program for Pollution Control in the Tanning Industry in South-East Asia.
4. A. J. Motheo and L. Pinhedo, Sci. Total Environ, 2000, 256, 67–76.
5. C. A. Basha, P. A. Soloman, M. Velan, N. Balasubramanian and L. R. Kareem, Ind. Eng. Chem. Res., 2009,48, 9786–9796.
6. Leather Industry Development Institute (LIDI) and United Nation Development Program (UNID), July, 2010, Processing of National work shop on enhancing the Ethiopia Leather Industry and its Market Competitiveness, Adama, Ethiopia.
7. JOURNAL OF FOREST PRODUCTS & INDUSTRIES, 2014, 3(3), 141-150
8. Treatment of Organics Containing from Leather Processing Unit using Electro–Oxidation – A Noval Approach, P. Vijayalakshmi* and P. Sarvananan, 2015, International Journal of Chem Tech Research CODEN (USA): IJCRGG ISSN: 0974-4290, Vol.7, No.7, pp 3004-3012, 2015.
9. Dr. S Rajamani, World Environmental Update in Leather Sector - Bio-Energy Generation from Tannery Effluent and Solid Wastes, Leather News India, September 2010
10. J. Kanagraj, Velappen K.C., Chandra Babu N.K., Sadulla S., Solid Wastes Generation in The Leather Industry and Its Utilization for Cleaner Environment-A Review, Journal of Scientific and Industrial Research, 65, 2006, 541-548.
11. Bio-info Publications, International Journal of Agriculture Sciences, ISSN: 0975-3710, Volume 1, Issue 2, 2009.
12. Treatment of tannery wastewater by a hybrid electro coagulation/ electro analysis process, AbdalhadiDeghles, Ugur Kurt; Department of Environmental Engineering, Yildiz Technical University, 34349 Istanbul, Turkey, 2016

13. V. Suresh, M. Kanthimathietal. An Improved Product-Process for Cleaner Chrome Tanning in Leather Processing, Journal of Cleaner Production 9 (2001) 483–491

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

15. Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques for the Tanning of Hides and Skins, May 200, European Commission Directorate-General JRC Joint Research Centre, Institute for Prospective Technological Studies (Seville), Technologies for Sustainable Development, European IPPC Bureau

16. Palanisamy Thanikaivelan et al, Recent Trends in Leather Making: Processes, Problems, and Pathways, Critical Reviews in Environmental Science and Technology, 35:37–79, 2005

17. Ramesh Bhadrinarayana, N.S., Meera S.B. and Anantharaman, N. (2007).Treatment of tannery wastewater by electrocoagulation. Chem. Techn. Metallurgy, 42(2), 201-206

18. Kyung-Sok, M. JaeJeong, Y. and Zuwhan, Y. (2004). Removal of ammonium from tannery wastewater by electrochemical treatment. Envron. Sci. Health, 39(7), 1867 – 1879

19. Lefebvre, O., Vasudevan, N., Thanasekaran, K.and Moletta, R. (2006). Anaerobic digestions of tannery soak liquor with an aerobic post-treatment. Wat. Res. 40, 1492 – 1500.

20. Metes, A., Kovacevic, D., Vujevic, D. and Papic, S. (2004). The role of zeolites in wastewater treatment of printing inks. Wat. Res., 38(14), 3373–3381.

21. EPA (2003). Provisional Standards for Industrial Pollution Control in Ethiopia: ESID Project, US/ETH/99/068/Ethiopia, EPA/UNIDO, Addis Ababa.;

22. UNEP (2004). Technical Guidelines on Hazardous Wastes physico-Chemical Treatment, Biological Treatment. Basel Convention Series/SBC No: 99/007, Geneva.

23. Linda, A. L. and Peter K. J. (1999). Physico-chemical treatment methods for the removal of microcystins (cyanobacteria hepatotoxins) from potable waters. Chem. Soc. Rev., 28, 217–224.).

24. Haydar S, Aziz JA (2009) Coagulation–flocculation studies of tannery wastewater using combination of alum with cationic and anionic polymers. J Hazard Mater 168(2-3): 035–1040.

25. R. Cassano, R. Molinari, M. Romano, E. Drioli, Treatment of aqueous effluents of the leather industry by membrane processes, J. Membr. Sci. 181 (1) (2001) 111–126.;

26. Awan, A. M. (2004). Reduction of chemical oxygen demand from tannery wastewater by Oxidation. EJEAF Che. 3(1), 625-628

27. Ramesh. Bhadrinarayana, N.S., Meera S.B. and Anantharaman, N. (2007).Treatment of tannery wastewater by electrocoagulation. Chem. Techn. Metallurgy, 42(2), 201-206

28. Metcalf and Eddy, Inc. (1991) “Wastewater Engineering”: Treatment Disposal and Reuse, third edition. New York: McGraw-Hill

29. Seungmoon, L., Sanjeev, M., Jung-Hwa, J. and Kwinam, P. (2006). Development of physicochemical nitrogen removal process for high strength industrial wastewater. Wat. Res., 20, 975 – 980.

30. Sarioglu M. (2005). Removal of ammonium from municipal wastewater using natural Turkish (Dogantepe) zeolite. Purif. Technol., 41(1), 1–11.;

31. Metes, A., Kovacevic, D., Vujevic, D. and Papic, S. (2004). The role of zeolites in wastewater treatment of printing inks. Wat. Res., 38(14), 3373–3381.

32. Del Pozo, R. and Diez, V. (2003). Organic matter removal in combined anaerobic–aerobic fixed-film bioreactors. Wat. Res. 37, 3561–3568

33. Pittier, P. and Chudoba, J. (1990). Biodegradability of Organic Substances in the aquatic Environment, CRC Press.;

34. Ahn, D.H., W.S. Chang and T.I. Yoon, 1999. Dyestuff wastewater treatment using chemical oxidation, physical adsorption and fixed bed biofilm process. Process Biochem, 34: 429-439.;

35. Chandra, P., Sinha, S. and Rai, U.N. 1997. Bioremediation of Cr. from water and soil by vascular aquatic plants. ACS Sympopsium, series, vol. 664, Washington, p. 274-282.;

36. Bashaar, Y. A. (2004). Nutrients requirements in biological industrial wastewater treatment. African Journal of Biotech, 3 (4), 236-238.

37. Ahn, D.H., W.S. Chang and T.I. Yoon, 1999. Dyestuff wastewater treatment using chemical oxidation, physical adsorption and fixed bed biofilm process. Process Biochem, 34: 429-439.;

38. Metcalfm and Eddy (2003). Wastewater Engineering: treatment and reuse, 4th, Mc GrawHil Boster;

39. EPA (2003). Provisional Standards for Industrial Pollution Control in Ethiopia: ESID Project, US/ETH/99/068/Ethiopia, EPA/UNIDO, Addis Ababa.

40. Jayaseelan S. (1997). A simple mathematical model for anaerobic digestion process. Wat. Sci. Tech. 35,185-191.;

41. S. Haydar, J. Anwar Aziz, J. Hazard. Mater. 168 (2009) 1035–1040.

42. Nicholas P. C. (1996).Biotechnology for Waste and Wastewater Treatment. Weatwood, New Jerary, U.S.A.

43. Seabloom, R.W. and Buchanan, J.R (2005). Aerobic Treatment of Wastewater and Aerobic Treatment. National Decentralized Water Resources Capacity Development Project. University of Arkansas, Fayetteville, AR.;

44. Boari, G., Mancini, I.M. and Trulli, E. (1997). Technologies for water and wastewater treatment. Università degli Studi Della Basilicata, Potenza, Italy.

45. Venkata Rao P., and Puvanakrishnan, R., (1993), Sci. Rep, 30, pp. 58-61.

46. Ganesh, R. and Ramanujam, R.A. (2009) 'Biological waste management of leather tannery effluents in India: current options and future research needs', Int. J. Environmental Engineering, Vol. 1, No. 2, pp.165–186.

47. Farabegoli, G., A. Carucci, M. Majone and E. Rolle, 2004. Biological treatment of tannery wastewater in the presence of chromium. J. Environ. Manage. 71: 345-349.

48. Lefebvre, O., N. Vasudevan, M. Torrijos, K. Thanasekaran and R. Moletta, 2006. Anaerobic digestions of tannery soak liquor with an aerobic post-treatment. Water Res., 40: 1492-1500.

49. Sekaran, G., K. Chitra, M. Mariappan and K.V. Raghavan, 1996. Removal of sulphide in anaerobically treated tannery wastewater by wet air oxidation. J. Environ. Sci. Health A., 31: 579-598.

50. Ganesh, R. and Ramanujam, R.A. (2009) 'Biological waste management of leather tannery effluents in India: current options and future research needs', Int. J. Environmental Engineering, Vol. 1, No. 2, pp.165–186.

51. Krishanamoorthi S, Sivakumar V, Saravanan K, Prabhu TVS (2009) Treatment and Reuse of Tannery Waste Water by Embedded System. Modern Appl Sci 3(1): 129–134.

52. J. Feng and D. C. Johnson, J. Electrochem. Soc., 1990, 137, 507–510

53. Afonso, M., Geraldes, V., Rosa, M., and De Pinho, M., "Nano filtration Removal of Chlorinated Organic Compounds from Alkaline Bleaching Effluents in a Pulp and Paper Plant", Water Research, 26, 1639 (1992) ;

54. R. Cassano, R. Molinari, M. Romano, E. Drioli, Treatment of aqueous effluents of the leather industry by membrane processes, J. Membr. Sci. 181 (1) (2001) 111–126.

55. Marcucci et al 2002 Experimental campaigns on textile wastewater for reuse by means of different membrane processes .Elsevier 10 September 2002, Pages 137-143

56. Cartwright, P.S., "Zero Discharge/Water Reuse - The Opportunities for Membrane Technologies in Pollution Control", Desalination, 83, 225 (1991);

57. Sinisgalli P. and Mcnutt J., "Industrial Use Of Reverse Osmosis", Journal AWWA, 47 (1986);

58. Cartwright, P.S., "Zero Discharge/Water Reuse - The Opportunities for Membrane Technologies in Pollution Control", Desalination, 83, 225 (1991);

59. Rameshraja, D.; Suresh, S., (2011). Treatment of Tannery Wastewater by Various Oxidation and Combined Processes. Int. J. Environ. Res., 5(2): 349-360.

60. Chamarro E., Marco A., Esplugas S. (2001) Use of Fenton reagent to improve organic chemical biodegradability, Water Research, 35, 1047-1051.;

61. Lidia, S., Santosh, N. Kaul and Rao N. (2005).Tannery wastewater treatment by electro oxidation coupled with a biological process. App. Electrochemistry 35(4), 381-390;

62. Metcalf and Eddy, Inc. (1991) “Wastewater Engineering”: Treatment Disposal and Reuse, third edition. New York: McGraw-Hill

63. O. Weres and M. R. Hoffmann, US Pat., 5 419 824, 1995

64. Robinson T., Mcmullan G., Marchant R. and Nigam P., Remediation of Dyes In Textile Effluent: A Critical Review On Current Treatment Technologies With A Proposed Alternative, Colorage, 44, 247-255 (1997);

65. N. Mohan, N. Balasubramanian, C. Ahmed Basha, Electrochemical oxidation of textile wastewater and its reuse, J. Hazard. Mater. 147 (2001) 644–651.

66. Kobya, M., Can, O.T., Bayramoglu, M., 2003. Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes. J. Hazard. Mater. B 100, 163–178.

67. Lin, S.H., Shyu, C.T., Sun, M.C., 1998. Saline wastewater treatment by electrochemical method. Water Res. 32, 1059– 1066

68. G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41...

69. Rajeshwar K., Ibanez J.G., Swain G.M., (1997), J. Appl.Electrochem., 24, 1077. Bockris 1975; Genders and Weinberg 1992;

70. . Sequeira, C. A. C., in: Studies in environmental science 59, Elsevier, Amsterdam; New York, 1994, xxvii, 718 p.

71. Canizares P., Hernández-Ortega M., Rodrigo M.A., Barrera-Díaz C.E., Roa-Morales G., Sáez C. 2009. A comparison between conductive-diamond electrochemical oxidation and other advanced oxidation processes for the treatment of synthetic melanoidins. J. Hazard. Mater, 164, 120–125.

72. Mollah M.Y.A., Schennach R., Jose R.P. and David L.C., (2001), Electrocoagulation (EC) — science and application, Journal of Hazardous Materials, B84, 29–41.

73. Balasubramanian, N.; Kojima, T.; Srinivasakannan, C., (2009), Arsenic removal through electrocoagulation: Kinetic and statistical modeling. Chem. Eng. J., 155, 76-82.

74. Ignacio, G.J., Manuel, B., Pablo, C. and Manuel, J. B. (1995). Treatment of tannery effluents by a two-step Coagulation/Flocculation process. Wat. Res., 29(6), 2605- 2608.

75. Mollah MY, Morkovsky P, Gomes JA, Kesmez M, Parga J, COCKE DL. Fundamentals, present and future perspectives of electrocoagulation. J Hazard Mater 2004; 114: 199–210.).

76. Benefield, L. D. and Randall, C. W. (1985). Biological Process Design for Waste Water Treatment. Ibis Publishing, Charlottesville, Virginia.

77. Yuan, R., Ramjaun, S.N., Wang, Z. and Liu, J. (2011). Effects of chloride ion on 161 degradation of Acid Orange 7 by sulfate radical-based advanced oxidation process: Implications for formation of chlorinated aromatic compounds. Journal of hazardous materials 196, 173-179

78. Ugurlu M., Karaoglu M.H. 2011. TiO2 supported on sepiolite: Preparation, structural and thermal characterization and catalytic behavior in photo catalytic treatment of phenol and lignin from olive mill wastewater. Chem. Eng. J., 166, 859–867.

79. Brillas E., Sirés I., Oturan M.A., Electro-Fenton process and related electrochemical technologies based on Fenton s reaction chemistry. Chem. Rev., 109(12), 2009., pp. 6570-6631

80. Brillas E., Boye B., Sirés I., J.A. Garrido, R.M. Rodríguez, C. Arias, P.L. Cabot, Ch. Comninellis, Electrochim. Acta 49, 2004. p. 4487

81. I. Sirés, J.A. Garrido, R.M. Rodríguez, E. Brillas, N. Oturan, M.A. Oturan, Appl. Catal. B: Environ. in press

82. Buxton G.V., Greenstock C.L., Helman W.P., Ross A.B, J. Phys. Chem. Ref. Data 17, 1988. p. 513

83. Miled W., Said A., Roudseli S., Decolorization of High Polluted Textile Wastewater by Indirect Electrochemical Oxidation Process, JTATM, Vol. 6(3), 2010., p. 324

84. Shah Hardik V., Electrochemical Oxidation of Organic Pollutants, Chemical Engineering Department Sarvajanik College of Engineering and Technology.

85. Priambodo R., Yu-Jen S., Yu-Jen H., Yao-Hui H., Treatment of real wastewater using semi batch (Photo)- Electro-Fenton method, Sustain. Environ. Res., 21(6), 2011., pp. 389-393

86. Huitle C.A.M., Direct and indirect electrochemical oxidation of organic pollutants, Ph.D. thesis work, University of Ferrara, 2004.

87. C. Comninellis, A. Kapalka, S. Malato, S.A. Parsons, I. Poulios, D. Mantzavinos, Journal of Chemical Technology and Biotechnology 83, 2008., pp. 769-776

88. Birame B., Brillas E., Marselli B., Michaud P., Comninellis C., Marième D., Bull. Chem. Soc. Ethiop. 18(2), 2004, pp. 205-214

89. Comninellis, C., Pulgarin, C., 1993. Electrochemical oxidation of phenol for wastewater treatment using SnO2, anodes. J. Appl. Electrochem. 23, 108–112.

90. Comninellis, C., 1994. Electro catalysis in the electrochemical conversion/combustion of organic pollutants for waste water treatment. Electrochim. Acta 39, 1857–1862.

91. Lidia Szpyrkowicz, Santosh N. Kaul, Rao N. Neti & Shanta Satyanarayan, Influence of anode material on electrochemical oxidation for the treatment of tannery wastewater. Water Research, 39, pp. 1601-1613, 2005

92. N.N. Rao, K.M. Somasekhar, S.N. Kaul, L. Szpyrkoicz, Electrochemical oxidation of tannery wastewater, J. Chem. Tech. Biotech. 76 (2001) 1124–1131.

93. Sundarapandiyan S, Chandrasekar R, Ramanaiah B, Krishnan S, and Saravanan P, Electrochemical oxidation and reuse of tannery saline wastewater. Journal of Hazardous Material, (2010), 180, pp. 197–203

94. Min K. S, Yu J. J, Kim Y. J, and Yun Z, Removal of ammonium from tannery wastewater by electrochemical treatment, Journal of Environmental Science and Health, 2004, 39, pp. 1867–79.

95. Clesceri, L.S., Greenberg, A.E. and Trussel, R.R. Eds. (1989). In standard methods for the examination of water and wastewater, 17th ed, American public health association Washington DC

96. N.K. Chandrababu, Electrochemical oxidation and reuse of pickling wastewater from tanneries, J. Am. Leather Chem. Assoc. 103 (2008) 370–376.

97. American Public Health Association (APHA). 1995. Standard Methods for the Examination for Water and Wastewater (19th edition). Byrd Prepess Springfield, Washington.

98. Ivonne Linares-Hernández a, Carlos Barrera-Díaz a,∗, Bryan Bilyeub, Pablo Juárez GarcíaRojas a, Eduardo Campos-Medinac” A combined electrocoagulation–electrooxidation treatment for industrial wastewater” Journal of Hazardous Materials 175 (2010) 688–694

Annex

Annex 1: Daily soaking capacity of Ethiopian Leather Industries

Ref. No.	Name of Tannery	Soaking Capacity (pieces/day)		Soaking Capacity (tonne/day)	
		Skin	Hide	Skin	Hide
1	Addis Ababa Tannery	2500	900	3.25	18.9
2	Bahir Dar Tannery Plc.	2000	300	2.60	6.3
3	Batu Tannery Plc.	2500	1000	3.25	21
4	China Africa Tannery	12000		15.6	
5	Colba Tannery Plc.	6000	600	7.8	12.6
6	Debrebrehan Tannery	5000		6.5	
7	Dire Tannery	6000	600	7.8	12.6
8	East Africa tannery	7000		9.3	
9	ELICO	13000	1000	16.9	21
10	Ethiopia Tannery Share	12000	1200	15.6	25.2
11	Farida Tannery	7000		9.1	
12	Friendship Tannery	10000	1000	13	21
13	Gellan Tannery Plc.	3000		3.9	
14	Habesha Tannery	3000		3.9	
15	Hafde Tannery Plc.	6000	250	7.8	5.25
16	Hora Tannery Plc.	3000		3.9	
17	Kombolcha Tannery	6000		7.8	
18	Mersa Tannery Plc.	6000	300	7.8	6.3
19	Mesaco Global Tannery	2500		3.25	
20	Modjo Tannery Share Company	7000	500	9.1	10.5
21	Sheba Tannery	6000	600	7.8	12.6
22	Sun industrial Tannery	3000		3.9	
23	United vasn Tannery	3000		3.9	
24	Wallia Tannery Plc.	5000	500	6.5	10.5
Total		141,500	9,050	183.95	190.05

Source: Leather industry development institute and tanneries 2012/13 tannery soaking capacity performance.

Annexes II: Laboratory Procedures for Water and Wastewater Analysis.

i) BOD test

Biochemical oxygen demand represents the amount of oxygen consumed by bacteria and other living microorganisms in the stabilization of organic matter of water/wastewater. Bacteria biodegrade the organic matter under aerobic conditions at a specified temperature, this test determines the organic material present in wastewater.

The method consists of filling with sample, to overflowing, an airtight bottle of the specified size and incubating it at the specified temperature for 5 day. DO is measured initially and after incubation, and the BOD5 is computed from the difference between initial and final DO. Because the initial DO is determined shortly after the dilution is made, all oxygen uptake occurring after this measurement is included in the BOD measurement.

Five days biological oxygen demand measurements were carried out according to procedures given in standard methods for the examination of water and wastewater, 5 – days BOD test. [49].

Apparatus used

a) Incubation bottles: Use glass bottles having 60 ml or greater capacity (300 ml bottles having a ground glass stopper and a flared mouth are preferred). Clean bottles with a detergent, rinse thoroughly and drain before use.

b) Air incubator or water bath, thermostatically controlled at 20 ± 1°C. Exclude all light to prevent possibility of photosynthetic production of DO.

Required reagent

Prepare reagents in advance but discard if there is any sign of precipitation or biological growth in the stock bottles.

a) Potassium hydroxide (KOH) to absorb carbon dioxide gas (CO2)

b) Nitrification inhibitor, 2 – chlorine – 6 - (trichloromethyl) pyridine. To avoid nitrification

c) Dilution water: use demineralized, distilled, tap, or natural water for making sample dilutions

d) Acid and alkali solutions, 1 N of NaOH and HCl, for neutralization of caustic or acidic Wastewater samples.

Experimental procedures

Preparation of the sample

a) Select the volume for the wastewater sample

b) The sample volume is related to the expected BOD5value. The BOD5 incubator is designed to operate with the following BOD5ranges and sample volume allowing BOD5 measurement.

i) BOD5range 0 - 400 mg/l use the sample without dilution

ii) BOD5range0 –2000 mg/l, the expected sample volume is 56 ml with 3 drop of nitrification inhibitor and 3 -4 drop of potassium hydroxide (KOH) addition.

iii) BOD5range0 – 4000 mg/l the expected sample volume is 21.2ml with 1 drop of nitrification inhibitor and 3 -4 drop of potassium hydroxide (KOH) addition.

c) Carry out the necessary pretreatment of the wastewater sample, setting pH 6.5 - 7.5, if higher or lower adjust by HCl and NaOH and mix well and allow the sample to settle and filtrate of the sample

d) Measure the wastewater sample precisely using appropriate overflow and if necessary, add nitrification inhibitor

e) Insert magnetic stirring rod

f) Place 3 - 4 drop of KOH solution into the seal gasket and insert gasket in the neck of the bottle, screw the BOD sensors to the sample bottle and then place the bottle in the bottle rack

g) Finally, incubate the sample for 5 days at a temperature of 20^{0}C.

Calculation

For each test bottle meeting the 2.0 mg/l minimum dissolved oxygen (DO) depletion and the 1.0 mg/l residual DO, calculate BOD5as follows:

$$\mathrm{BOD5, mg/l} = \frac{\mathrm{D1} - \mathrm{D2}}{\mathrm{p}}$$

Where, D1= DO of diluted sample immediately after preparation, mg/l.

D2= DO of diluted sample after5 day incubation at 20 °C, mg/l.

P = decimal volumetric fraction of sample used.

ii) COD Analysis

The chemical oxygen demand is the amount of oxygen required to completely oxidize the organic matters and other chemical reducing substances of the wastewater. Chemical oxygen demand measurements were carried out according to procedures given in standard methods for the examination of water and wastewater, titrimetric method [49].

Apparatus used

Reflux apparatus, Burettes and pipettes

Required reagent

1. Standard potassium dichromate solution 0.25N.
2. Sulphuric acid reagent.
3. Standard ferrous ammonium sulphate.
4. Ferroin indicator solution.
5. Mercuric sulphate.
6. Sulphuric acid crystals.

Experimental procedures

1. Place 50.0ml of sample in a 500ml refluxing flask.
2. Add 1g mercuric sulphate and a few glass beads.
3. Add sulphuric acid to dissolve the mercuric sulphate and cool.
4. Add 25.0 ml 0.25 N potassium dichromate solution and mix well.
5. Attach the flask to the condenser and start the cooling water.
6. Add the remaining acid reagent (70ml) through the open of condenser and mix well.
7. Apply heat and reflux for 5 hours.
8. Cool and wash down the condenser with distilled water.
9. Dilute the mixture to about twice its volume and cool to room temperature.
10. Titrate the excess dichromate with standard ferrous ammonium sulphate using ferroin indicator. (2 to 3 drops).
11. The color change from blue green to reddish indicates the end point.
12. Reflux in the same manner a blank consisting of distilled water of equal volume as that of the sample.

Chemical oxygen demand concentration was calculated using the following formula:

$$\mathrm{COD}\ (\frac{\mathrm{mg}}{\mathrm{l}}) = \frac{(V1 - V2)}{V} N \times 8000$$

Where; V1= ml ferrous ammonium sulphate used for blank.

V2= ml ferrous ammonium sulphate used for sample.

N= normality of ferrous ammonium sulphate.

V= volume of sample used.

i. Total Dissolved Solids

General Discussion

a. Principle: A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids. This procedure may be used for drying at other temperatures. The results may not agree with the theoretical value for solids calculated from chemical analysis of sample (see above). Approximate methods for correlating chemical analysis with dissolved solids are available.1 The filtrate from the total suspended solids determination (Section 2540D) may be used for determination of total dissolved solids.

b. Interferences: See Section 2540A.2 and Section 2540B.1. Highly mineralized waters with a considerable calcium, magnesium, chloride, and/or sulfate content may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Samples high in bicarbonate require careful and possibly prolonged drying at 180°C to insure complete conversion of bicarbonate to carbonate. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue.

Apparatus

Apparatus listed in Section 2540B.2a - h is required, and in addition:

a. Glass-fiber filter disks without organic binder.

b. Filtration apparatus: One of the following, suitable for the filter disk selected:

1) Membrane filter funnel.

2) Gooch crucible, 25-mL to 40-mL capacity, with Gooch crucible adapter.

3) Filtration apparatus with reservoir and coarse (40- to 60-µm) fritted disk as filter support (48)

c. Suction flask, of sufficient capacity for sample size selected.

d. Drying oven, for operation at 180 ± 2°C.

Procedure

a. Preparation of glass-fiber filter disk: If pre-prepared glass fiber filter disks are used, eliminate this step. Insert disk with wrinkled side up into filtration apparatus. Apply vacuum and wash disk with three successive 20-mL volumes of reagent-grade water. Continue suction to remove all traces of water. Discard washings.

b. Preparation of evaporating dish: If volatile solids are to be measured, ignite cleaned evaporating dish at 550°C for 1 h in a muffle furnace. If only total dissolved solids are to be measured, heat clean dish to 180 ± 2°C for 1 h in an oven. Store in desiccator until needed. Weigh immediately before use.

C. Selection of filter and sample sizes: Choose sample volume to yield between 2.5 and 200 mg dried residue. If more than 10 min are required to complete filtration, increase filter size or decrease sample volume.

d. Sample analysis: Stir sample with a magnetic stirrer and pipet a measured volume onto a glass-fiber filter with applied vacuum. Wash with three successive 10-mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete. Transfer total filtrate (with washings) to a weighed evaporating dish and evaporate to dryness on a steam bath or in a drying oven. If necessary, add successive portions to the same dish after evaporation. Dry evaporated sample for at least 1 h in an oven at 180 ± 2°C, cool in a desiccator to balance temperature, and weigh. Repeat drying cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less. Analyze at least 10% of all samples in duplicate.

Calculation

$$\text{mg total dissolved solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

Where:

A = weight of dried residue + dish, mg, and

B = weight of dish, mg.

Annexes III: Model summary statistics

Response: COD

ANOVA for Selected Factorial Model

Analysis of variance table [Partial sum of squares]

	Sum of Squares	DF	Mean Square	F Value	Prob > F
Source Model	0.000				
Residual	4164.15	23	181.05		
Cor Total	4164.15	23			

Std. Dev.	13.46	R-Squared	0.0000
Mean	62.80	Adj R-Squared	0.0000
C.V.	21.43	Pred R-Squared	-0.0888
PRESS	4534.12	Adeq Precision	

A negative "Pred R-Squared" implies that the overall mean is a better predictor of **COD** response.

Response: BOD

ANOVA for Selected Factorial Model

Analysis of variance table [Partial sum of squares]

	Sum of Squares	**DF**	**Mean Square**	**F Value**	**Prob > F**
Source Model	0.000				
Residual	7475.08	23	325.00		
Cor Total	7475.08	23			

Std. Dev. 18.03 R-Squared 0.0000

Mean 50.37 Adj R-Squared 0.0000

C.V. 35.79 Pred R-Squared -0.0888

PRESS 8139.21 Adeq Precision

Response: TDS

ANOVA for Selected Factorial Model

Analysis of variance table [Partial sum of squares]

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**
Model	0.000				
Residual	745.32	23	32.41		
Cor Total	745.32	23			

Std. Dev. 5.69 R-Squared 0.0000

Mean 6.96 Adj R-Squared 0.0000

C.V. 81.78 Pred R-Squared -0.0888

PRESS 811.54 Adeq Precision

	Prediction	**SE Mean**	**95% CI low**	**95% CI high**	**SE Pred**	**95% PI low**	**95% PI high**
COD	62.8004	2.75	57.12	68.48	13.73	34.39	91.21
BOD	50.3678	3.68	42.76	57.98	18.40	12.31	88.43
TDS	6.96042	1.16	4.56	9.36	5.81	-5.06	18.98

Annexes IV: Appearance and Factors of Electro-Oxidation for treatment

During the electro-oxidation, the soaking liquor wastewater were rapidly converted organic pollutant into carbon dioxide and water Fig.4.3 a &b, shows the treated wastewater after electro-oxidation. The color of initial soaking liquor waste was Intense brown and high turbidity and after treating with electro-oxidation become looking a clear water and colorless.

a. Initial Soaking liquor b. Treated Soaking liquor

ii. Initial Soaking liquor ii. Treated Soaking liquor

Figure 4.3: -The color difference before and after treating with EO

a. Effect of Time on pollution reduction

The time of electro-oxidation plays a vital role in the degradation of the organic pollutant of soaking liquor wastewater samples. Fig. 4.4 provides the samples of electro-oxidation from the different batch processes at 30-minute different time intervals.

Figure 4.4: - The color change and the electro-oxidation process with the interval of 30 minute.

b. Effect of pH Effect on pollution reduction

The pH of the solution was maintained between 6 and 9. The results obtained at this 2 different pH's are depicted in Fig. 4.5. It is seen the product obtained at a pH of 6 was clearer than that obtained at a pH of 9.

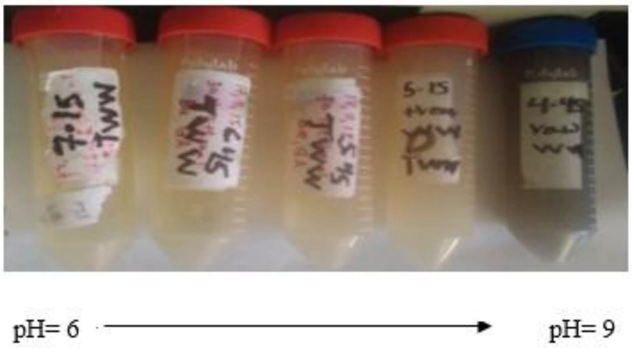

Figure 4.5: -pH variation during electrochemical oxidation treatment within different time interval.

The process standardization of electro-oxidation of tannery saline wastewater at the soaking stage was carried out by studying the effects of pH, current density, salt concentration and electrolysis time. For these studies, the soaking saline tannery wastewater was used. Initial COD, BOD, and TDS of the prepared soaking liquor wastewater are 2056mg/L, 661 mg/L and 6510 mg/L respectively.

For the first set of experiments, pH had been varied from 6 to 9. Current density and NaCl concentration were kept at constant. COD was reduced by 34.11 % and 69.88 % at pH 7.81and pH 6.50 respectively. The rate of COD reduction and TKN reduction concerning time is shown

Annexes V: Effect of different parameters on wastewater parameter (COD, BOD & TDS

Figure C .1 Normal plots of residuals for adsorption of COD (mg/l)

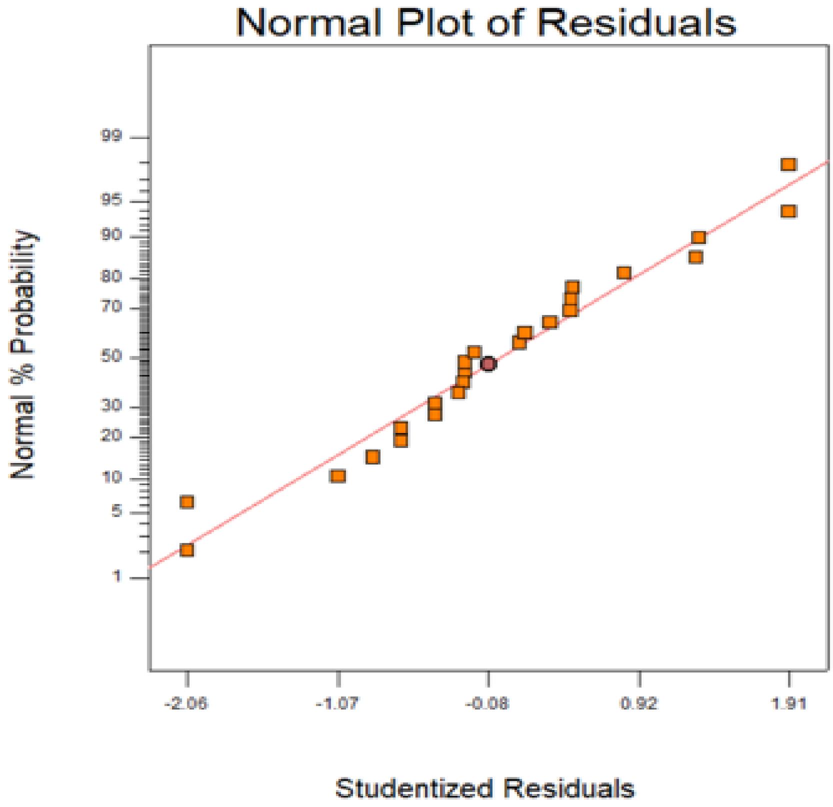

Figure C .2 Normal plots of residuals for adsorption of BOD (mg/l)

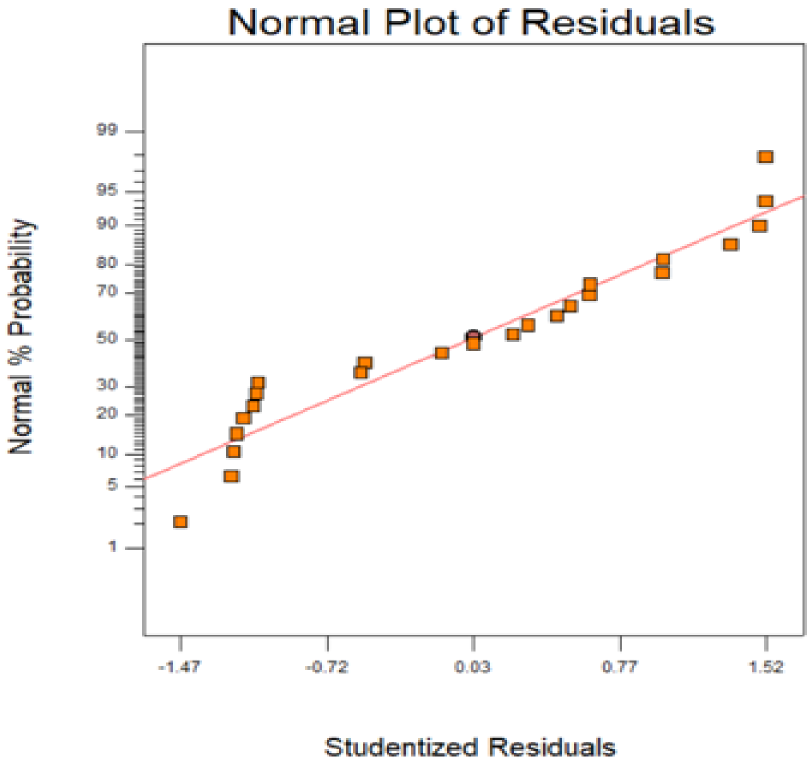

Figure C .3 Normal plots of residuals for adsorption of TDS