# Sudan University of Science and Technology College of Graduate Studies

# Performance Evaluation of Industrial Waste Water Treatment Plant of White Nile Tannery

تقويم أداء محطة معالجة المياه العادمة بمدبغة النيل الأبيض

A thesis submitted to the graduate faculty of Sudan University of Science and Technology in partial fulfillment of the requirements for degree of MSc in Environmental Engineering

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# Dedication

I dedicate this study with my love to my parents ,brothers ,sisters ,teachers and all my friends for their continuous direct and indirect support ,patience and encouragement throughout the different stages of this work.

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Ш

# Abstract

One of the most hazardous pollutants to the environment is those produced from the industrial activities, and tanneries are one of the sources of the environmental pollution for their production of toxic and carcinogenic wastes such as chromium. The main objective of this study was to assess the performance of the industrial wastewater treatment plant of White Nile tannery. The performance was evaluated in terms of the characteristics of the wastewater disposing in the sewage network after passing through the primary treatment plant, such as biological oxygen demand(BOD), chemical demand(COD),total suspended solid(TSS),total oxygen dissolved solid(TDS), oil and greases, PH, and chrome(Cr). the results obtained showed that the minimum concentration of BOD, COD, TDS and pH after treatment are (620, 1600,5820 mg/l and 7) respectively, these values doesn't meet the requirement of the Sudanese standards for the disposal of industrial wastewater in the sewage network except the TSS, the maximum concentration of TSS it is 340 mg/l . So the high values of BOD and COD after treatment compared with the standard limits indicate that the biological treatment is not efficient, therefore The BOD and COD removal efficiency should be increased by mixing sewage with industrial wastewater to increase the amount of microorganisms, and the duration of treatment should be increased also from 16 hr to 32 hr to reduce concentrations of organic pollutants, but the sedimentation process works efficiently according to TSS values. There is a variation in Cr values, some values meet the requirement of the Sudanese standard and others are higher than the allowable limit, therefore, there is a need for a unit in the treatment plant to recover the chromium (Cr) and reuse of it in the tanning process again.

المستخلص

أحد الملوثات الأكثر خطورة على البيئة هي تلك الناتجة عن الأنشطة الصناعية ، والمدابغ هي واحدة من مصادر التلوث البيئي لإنتاجها من النفايات السامة والمسببة للسرطان مثل الكروم. كان الهدف الرئيسي من هذه الدراسة هو تقييم أداء محطة معالجة مياه الصرف الصناعي في مدبغة النيل الأبيض. تم تقييم الأداء من حيث خصائص المياة المتخلص منها في شبكة الصرف الصحي بعد المرور عبر محطة المعالجة الأولية ، مثل الطلب على الأكسجين البيولوجي (BOD) ، والطلب على الأكسجين الكيميائي (COD) ، والمواد الصلبة العالقة الكلية (TSS) ، إجمالي الذائب الصلبة (TDS) و الرقم الهيدوجيني (PH)والكروم (Cr). أظهرت النتائج التي تم الحصول عليها أن الحد الأدني لتركيز BOD ، BOD، TDS ودرجة الحموضة بعد العلاج هي (620 ، 1600 ،5820 ملغ / لتر و 7) على التوالي ، هذه القيم لا تلبى متطلبات المعايير السودانية للتخلص من مياه الصرف الصناعي في شبكة الصرف الصحي باستثناءTSS والتركيز الاعلى ل TSS هو 340 ملغ/لتر. لذلك فإن القيم العالية للـ BOD و COD بعد المعالجة مقارنة بالحدود القياسية تشير إلى أن المعالجة . البيولوجية ليست فعالة ، لذلك يجب زيادة كفاءة ازالة ال BOD وCOD بخلط مياه الصرف الصحى بالمياه الصرف الصناعي لزياة كمية الاحياء الدقيقة بالاضافة الى زيادة زمن المعالجة من 16ساعة الى 32 ساعة لتقليل تراكيز الملوثات العضوية ، في حين أن عملية الترسيب تعمل بكفاءة وفقًا لقيم TSS. هناك تباين في قيم الكروم ، بعض القيم تلبي متطلبات المواصفات السودانية والبعض الآخر أعلى من الحد المسموح به ، وبالتالي هناك حاجة لوحدة في محطة المعالجة لاستعادة الكروم (Cr) وإعادة استخدامها في عملية الدباغة مرة أخرى.

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# Abbreviations

BOD	Biochemical oxygen demand.
CI <sup>-</sup>	Chloride
COD	chemical oxygen demand
Cr	Chrome.
ICP	Inductively coupled plasma.
NH <sub>3</sub>	Ammonia
O&G	Oils and greases.
РН	Power of hydrogen.
$S^{-2}$	Sulphur
TDS	Total dissolved solids.
TSS	Total suspended solids

# Chapter one Introduction

# **1.1 Introduction**

Industries have been fingered as the major institutions since the last four decades, responsible for diverse environmental and human catastrophes; hence they are a major contributor to environmental degradation and pollution. Environmental pollution due to appreciating industrial activities is unquestionably some of the most important problems of this century [A. U. Itodo, 2018].

Industrial pollution is a growing concern of the present days, wastes from industrial activities includes liquid wastewater or effluent, gaseous emissions and solid wastes [S. Obaidullah and A. L. Mahmood, 2008].

Major water pollution problems arise from industrial activities particularly from distillery, paper mills, tannery, sugar factories, dairy, fertilizer units, refineries, petrochemical industries, etc. The waste materials from these industries are characterized by high oxygen demand, total dissolved solids and hazardous inorganic chemical wastes [M. A. Mohamed, 2012].

Tanning is one of the oldest industries in the world; skin tanning is defined as art and technology that transforms animal skins into tanned skins resistant to biodegradation. But tanning industry represents one of the main sources of hazardous wastes [M. Mwinyihija, 2012].

Water is the basis for tanning, so it should be supplied in tanneries. Water is used to compensate for the loss of water from the water during the storage process as well as for the removal of blood, fouling, salt and other soluble substances.

1

According to the World Health Organization, tanning tons of skin it is expected to produce 52 cubic meters of waste water containing many pollutants such as blood, tanning industry also has one of the highest toxic intensity per unit of output. During tanning process at least about 300 kg chemicals are added per ton of hides. Tannery effluent is among one of the most hazardous pollutants of industry. Major problems are due to wastewater containing heavy metals, toxic chemicals, chloride, lime with high dissolved and suspended salts and other pollutants. The table below shows the values of pollution elements in effluents for tons of tanned leather (leather and tanning sector in the Arab world - Arab Labor Organization - Arab Institute for Occupational Health and Safety 1999)

 Table (1-1): The values of pollution elements in effluents for tons of tanned
 leather

Parameters	Concentration (mg/l)
BOD	75-90
COD	200-220
TSS	140
TDS	252
Cr	4
SO <sub>4</sub>	9
Oil and greases	19

Tannery wastewater treatment is complex due to the variety of chemicals added at different stages of processing of hides and skins. Major problems in tanneries are

due to wastewater containing heavy metals, toxic chemicals, chloride, lime with high dissolved and suspended salts and other pollutants.

Many conventional processes were carried out to treat wastewater from tannery industry such as biological process, oxidation process and chemical process etc. Among these, physical and chemical methods are considered very expensive in terms of energy and reagents consumption and generation of excessive sludge. The main advantages of biological treatment methods are

i. Low capital and operating costs compared to alternatives such as chemical-

oxidation processes.

- ii. True destruction of organics, versus mere phase separation, such as with air stripping or carbon adsorption.
- iii. Oxidation of a wide variety of organic compounds.
- iv. Removal of reduced inorganic compounds, such as sulphides and ammonia, and total nitrogen removal possible through denitrification.
- v. Operational flexibility to handle a wide range of flows and wastewater characteristics.
- vi. Reduction of aquatic toxicity <sup>(5)</sup>.

Therefore, it is necessary to do the primary treatment plant to removal hazardous pollutants before drainage to network. Therefore, the Sudanese standards set certain standards and values for the results of the environmental tests for industrial wastewater after the primary treatment, which allows for discharge in the sewage network.

## **1.2. Problem statement:**

The water produced by leather tanning contains a number of pollutants such as greases, sulfates, chlorides, chromium salts and other hazardous pollutants. Disposal of this industrial waste water without treatment in water resources or rivers leads to contaminate of aquatic environment also drainage with domestic waste water leads to damage of microorganisms used in biological treatment, therefore, it is necessary to be existed a primary treatment plant to remove the hazardous pollutants before drainage to sewage network, and the plant should operate efficiently to ensure that these hazardous pollutants are treated. In this research, we will evaluate the performance of the primary treatment plant for the White Nile tannery through treated wastewater discharge characteristics and ensure that it meets the specifications of disposal in the sewage network.

# **1.3. Objectives:**

## 1.3.1. General objective:

To assess the performance of the industrial wastewater treatment plant of White Nile tannery

## **1.3.2. Specific objectives:**

1. To evaluate whether or not the wastewater treatment plant is achieving its targeted efficiencies with respect to major pollution parameters include COD.BOD, TSS, TDS, PH, Cr, oil and greases.

2- To ensure that the discharged water meet the Sudanese industrial wastewater specifications of disposal in the sewage network.

3. To suggest corrective measures if the wastewater discharge specifications are not met.

# **Chapter Two**

# Literature review

## **2.1 Introduction**

Major water pollution problem arise from industrial activities particularly from distillery, paper mills, tannery, sugar factories, dairy, refineries, and petrochemicals industrials [M. A. Mohamed, 2012].

Industrial pollution is a growing concern of the present days. Wastes from industrial activities include liquid wastewater or effluent, gaseous emissions and solid wastes. Effluents are having the most devastating effects on people and the environment. Effluents, mostly untreated, are primarily discharged into rivers and streams. Since the water bodies are used for drinking, washing, domestic purposes, as well as irrigation and fisheries, pollution of the natural water bodies from industrial discharges is having the most damaging effect on the environment [S. Obaidullah and A. L. Mahmood, 2008].

Tanning is the process of transforming animal skins (a natural renewable resource) to leather (a market material used in the manufacture of a wide range of products). Tanning is claimed to be the second oldest profession in the world. In ancient times, tanning was considered as a noxious trade. However the industry has evolved with time. The leather industry is now recognized as a major industry of great economic importance on an international scale producing a host of products in one of the world's finest natural materials. Tanning industry is sometimes criticized on environmental grounds, although the only other viable alternative of dumping the putrefying hides and skins can be more hazardous and can cause even more severe environmental damage. Leather is a globally acclaimed product and there is an ever increasing demand for leather and its related products. The current

trade value of the leather industry is estimated to be approximately US\$ 70 billion per year. The industry in total produces about 18 billion square feet of leather a year, with developing countries producing over 60% of the world's leather. About 65% of the world production of leather is estimated to go into leather footwear. Its major expansion has taken place in developing and newly industrialized countries rather than in developed economies. In developing and newly industrialized countries solid waste and wastewater treatments are not state of the art and there is a high labor content to the processes involved in the conversion of hides and skins into leather. The United States, Germany, and other European countries remain major importers of leather products. Countries such as China India, Thailand, and Indonesia dominate the export of leather and leather products [R. A. Ramanujam, R. Ganesh, and J. Kandasamy, 2010].

Leather industry is a wide common worldwide and it can be a dominant regional player in certain areas of the world. This manufacturing industry consists of several different processes, one of the most important activities being the tanning of the raw hides. Tanning processes are considered to be one of the most polluting industrial activities in the world. It involves the processing of raw materials (animal skin) in order to make it stronger for use in a variety of different products. The tanning process can be represented in three main phases: acquisition and pre-treatment of raw animal hides; treatment of the hides with a tanning agent; and drying and shining the hides before sending them to product manufacturers. The two main types of tanning are chrome tanning and vegetable tanning, with chrome tanning making up a large majority of the industry [F. Giaccherini, 2016].

Manufacturing of leather goods, leather boards and fur produces numerous byproducts, solid wastes, high amount of wastewater containing different loads of pollutants and emissions into the air. The uncontrolled release of tannery effluents to natural water bodies increase health risks for human beings and environmental pollution. Effluents from raw hides processing tanneries, which produce wet-blue, crust leather or finished leather, contain compounds of trivalent chromium and sulphides in most cases. Organic and other ingredients are responsible for high BOD (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand) values and Represent an immense pollution load, causing technical problems, sophisticated technologies and high cost in concern of effluent treatment.

Nowadays chrome tanning is favored by the majority of the leather industry because of the speed of processing, low cost, color of leather and greater stability of the resulting leather. Uptake of the chromium into the leather is not complete and relatively large amount are found in the effluent estimates range IQ. From 2,000 - 3,000 mg/I to 3 - 350 mg/l. If these wastewaters are not treated before discharge, they can cause serious environmental pollution.

Treatment of this wastewater is expensive, and poorer country usually employs an initial treatment. Primary treatment may employ biological, oxidation, or physicochemical processes. These treatments often leave chromium level in the wastewater above the legal discharge limit for surface water, for tannery industry is I mg/I. Therefore, further treatment of chromium is required before ultimate discharge [S. Obaidullah and A. L. Mahmood, 2008].

## 2.2 Leather tanning industry

Leather is originated from animals used in the food industry. The great parts of the animals processed in the tanning industry are: lamb, goat, bovine, pork and mutton. However, only bovine, sheep and goat leathers are the most common worldwide. Data sets on leather production were gathered from Un-Fao, 2013 repositories and reported in Table 2-1.

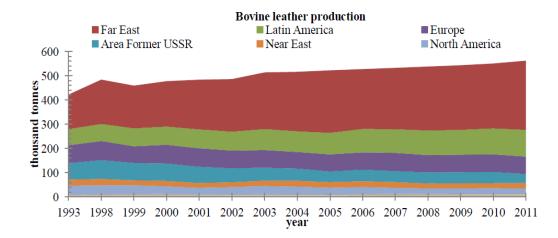
# Table2- 1: Global leather productions, 2011 UN- FAO (2013) [F. Giaccherini,

### 2016].

Country	Bovine leather production (tones per year)	Sheep and goat leather production (tones per year)
Latin American and	110000	16
Caribbean		
Africa	5000	49
Near East	22000	98
Far east	285000	225
North America	21000	6
Europe	71000	73
Rest of Europe	400	1
Area Former USSR	38000	22
Oceania Developed	3000	6
Developed Other	6000	0.3
World	562000	496

As shown in table2-1, all over the world the bovine leather production is the most important with 562 103 ton per year compared to 496 ton per year of the sheep and goat one.

Figure 1 shows the bovine leather production trend from 1993 to 2011 in the World.



**Figure 2-1:** Bovine leather production trend from hide to leather stock from 1993 to 2011, UN-FAO (2013) [F. Giaccherini, 2016].

Globally it shows a positive trend due to the increasing production in the Far East and Latin America. A mild decrease is present in the other areas of the world only partially correlated with the last year's economical crisis.

## **2.3 Tanning process**

Leather tanning is the process of converting raw hides or skins into leather. Hides and skins have the ability to absorb tannic acid and other chemical substances that prevent them from decaying, make them resistant to wetting, and keep them supple and durable. The surface of hides and skins contain hair and oil glands and is known as the grain side. The flesh side of the hide or skin is much thicker and softer. The three types of hides and skins most often used in leather manufacture are from cattle, sheep and pigs. Tanning is essentially the reaction of collagen fibers in the hide with tannins, chromium, alum, or other chemical agents. The most common tanning agents used in most tanneries is trivalent chromium and vegetable tanning agents extracted from specific tree barks. Alum, syntans (manmade chemicals), formaldehyde, glutaraldehyde and heavy oils are other tanning agents [M. A. Mohamed, 2012].

# 2.4 Process description

As shown in figure 2-2 the first operation, preservation, is usually carried out in the slaughterhouse before the shipping of the raw material to the tanneries.

Six main operations in the process from raw hides to leather stock: soaking-liming; dehairing; fleshing; pre-tanning; tanning; drying and finishing operations.

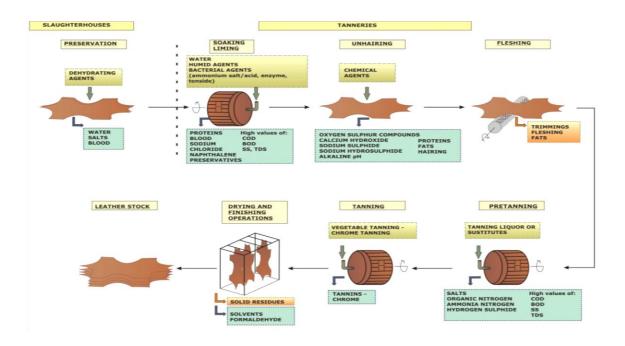


Figure 2-2: Tanning processes scheme [F. Giaccherini, 2016].

**1. Soaking and liming:** through water, humid and bactericidal agents (such as ammonium salt, acids, enzyme and tenside), and the raw hide regains their normal water contents. It is within this stage that high volume of water used consequently results to high discharge of effluent with high pollutant load. The discharge is rich on: proteins, blood, sodium chloride, naphthalene, preservatives and characterized by high values of chemical oxygen demand COD, biochemical oxygen demand BOD, suspended solids SS, total dissolved solids TDS. It is estimated that for processing 1 ton of raw skins (weight of skins before soaking), the input in a

typical input audit processing (kg) of lime is 100 with an output of 12.3, while Na2S has an input of 35 with an output of 18.3.

**2. Dehairing:** the process is done by chemical dissolution of the hair and epidermis with an alkaline medium of sulphide and lime. The wastewater is rich of oxygen sulphur components, calcium hydroxide, sodium sulphide, sodium hydrosulphide, alkaline pH, proteins, fats and hairing.

**3. Fleshing and trimming**: weak organic acids, digestive enzymes and inorganic acids, respectively, are used to remove lime, digest and remove the non-structural proteins and eventually bring the pH to a level that will enhance the tanning process.

4. Pre-tanning: this process commonly includes two sub-processes.

**a. Bating:** the dehaired, fleshed and alkaline hides are neutralised (deliming) with acid ammonium salts and treated with enzymes, similar to those found in the digestive system, to remove hair remnants and to degrade proteins. During this process hair roots and pigments are removed. The hides become somewhat softer by this enzyme treatment.

**b. Pickling:** this process increases the acidity of the hide to a pH of 3, enabling chromium tannins to enter the hide. Salts are added to prevent the hide from swelling. For preservation purposes, 0.03-2.00 weight percent of fungicides and bactericides are applied.

**5. Tanning:** this process can be done throughout the utilization of two different tanning agents, chrome tanning or vegetable tanning [F. Giaccherini, 2016].

**a. Chrome tanning:** Chrome-tanned leather tends to be softer and more pliable than vegetable- tanned leather. It has higher thermal stability, more stable in water,

and takes less time to produce than vegetable tanned leather. Almost all leather made from lighter-weight cattle hides and from the skin of sheep, lambs, goats, and pigs is chrome tanned. The first steps of the process (soaking, fleshing, liming/dehairing, deliming, bating, and pickling) and the drying/finishing steps are essentially the same as in vegetable tanning. However, in chrome tanning, the additional processes of retaining, dyeing, and fatliquoring are usually performed to produce usable leathers and a preliminary degreasing step may be necessary when using skin, such as sheepskin.

Chrome tanning is a process that is based on the reaction between the hide and a trivalent chromium salt, usually a basic chromium sulphate. In the typical one bath process, the hides are in a pickled state at a pH of 3 or lower, the chrome tanning materials are introduced, and the pH is raised. Following tanning, the chrome-tanned leather is piled down, wrung and graded for the thickness and quality, split in to flesh and grain layers and shaved to the desired thickness. The grain leather from the shaving machine is then separated for retanning, dyeing, and fatliquoring. Leather that is not subject to scuffs and scratches can be dyed on the surface only. For other types of leather (i.e., shoe leather) the dye must penetrate further into the leather.

Typical dyestuffs are aniline-based compounds that combine with the skin to form an insoluble compound. Fatliquoring is the process of introducing oil into the skin before the leather is dried to replace the natural oil lost in beam

House and tanyard processes. Fatliquoring is usually performed in a drum using an oil emulsion at temperature of about 60 to 660 C for 30 to 40 minutes. After fatliquoring, the leather is wrung, set out, dried, and finished. The finishing process refers to all the steps that are carried out after drying.

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After pickling, when the pH is low, chromium salts (Cr3+) are added. To fixate the chromium, the pH is slowly increased through addition of a base. The process of chromium tanning is based on the cross-linkage of chromium ions with free carboxyl groups in the collagen. It makes the hide resistant to bacteria and high temperature. The chromium-tanned hide contains about 2-3 dry weight percent of Cr3+. Wet blue, i.e. the raw hide after the chrome-tanning process, has about 40 percent of dry matter

**b.** Vegetable tanning: Heavy leathers and sole leathers are produced by the vegetable tanning process, the oldest of any process in use in the leather tanning industry. The hides are first trimmed and soaked to remove salt and other solids and to restore moisture lost during curing. Following the soaking, the hides are fleshed to remove the excess tissue to impart uniform thickness, and to remove muscles or fat adhering to the hide. Hides are then dehaired to ensure that the grain is clean and the hair follicles are free of hair roots. Liming is the most common method of hair removal, but thermal, oxidative, and chemical methods also exist. The normal procedure for liming is to use a series of pits or drums containing lime liquors (Calcium hydroxide) and sharpening agents. Following liming, the hides are dehaired by scraping or by machine. Deliming is then performed to make the skins receptive to vegetable tanning. Bating, and enzymatic action for the removal of unwanted hide components after liming, is performed to impart softness, stretch ability and flexibility to the leather. Bating and deliming are usually performed together by placing the hides in an aqueous solution of ammonium salt and proteolytic enzymes. In the vegetable tanning process, the concentration of the tanning materials starts out low and is gradually increased as the tanning proceeds. It usually takes 3 weeks for the tanning material to penetrate to the centre of the hide. The skins or hides are then wrung and may be cropped or split, heavy hides

may be retanned and scrubbed. For sole leather, the hides are commonly dipped in vats or drums containing sodium bicarbonate or sulphuric acid for bleaching and removal of surface tannins. Materials such as lignosulphate, corn sugar, oils, and specialty chemicals may be added to the leather. The leather is then set out to smoothen and dry; and may then undergo further finishing steps. However, a high percentage of vegetable-tanned leathers do not undergo retanning, colouring, fat liquoring or finishing.

Vegetable tanning is usually accomplished in a series of vats (first the rockersection vats in which the liquor is agitated and second the lay-away vats without agitation) with increasing concentrations of tanning liquor. Vegetable tannins are polyphenolic compounds of two types: hydrolysable tannins (i.e. chestnut and myrobalan) which are derivatives of pyrogallols and condensed tannins (i.e. hemlock and wattle) which are derivatives from catechol. Vegetable tanning probably results from hydrogen bonding of the tanning phenolic groups to the peptide bonds of the protein chains. In some cases as much as 50% by weight of tannin is incorporated into the hide [M. A. Mohamed, 2012].

**c. Finishing operations**: Chromium tanned hides are often re-tanned during which process the desirable properties of more than one tanning agent are combined and treated with dye and fat to obtain the proper filling, smoothness and color. Before actual drying is allowed to take place, the surplus water is removed to make the hides suitable for splitting and shaving. Splitting and shaving is done to obtain the desired thickness of the hide. The most common way of drying is vacuum drying. Cooling water used in this process is usually circulated and is not contaminated.

**d. Crust:** The crust that results after re-tanning and drying is subjected to a number of finishing operations. The purpose of these operations is to make the hide softer

and to mask small mistakes. The hide is treated with an organic solvent or water based dye and varnish. The finished end product has between 66 and 85 weight percent of dry matter [F. Giaccherini, 2016].

# 2.5 Tannery effluent

Tannery effluent is one of the most polluting industrial wastes. Leather production requires large amount of water (35 liter of water is consumed per kilogram of raw material processed). Tanning of hides and skins need to chemicals substances and, not more than 20% of the chemicals are absorbed by leather; the remainder flows out with the effluent.

Effluent from tannery is the most polluting and has high concentration of proteins, chlorides, trivalent chromium, nitrogen, sulphate, sulphides, COD, BOD and suspended solids. Volume and characteristics of wastewater discharged vary from process to process, tannery to tannery and from time to time. The operations in a tannery are done in batches and discharge of wastewater is also intermittent. Wastewater from beam house operations like soaking, liming, deliming, bathing etc., is alkaline and contains decomposable organic matter, hair, lime, TSS, TDS, sulphides and BOD. This is mainly due to the poor quality of calcium hydroxide and other chemicals used in excess without proper control.

Wastewater from vegetable tanning has high organic matter and wastewater from chrome tanning has large quantity of chromium since only 50 to 70% of Basic Chromium Sulphate (BCS) is taken up by leather and the balance is discharged in the waste [M. A. Mohamed, 2012].

Figure (2-3): show the tanning process and pollutants produced from this process.

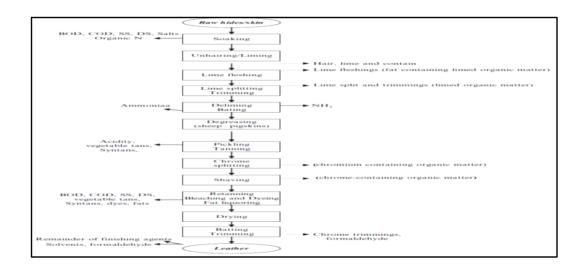


Figure (2-3): tanning process and pollutants produced from the process [H. Dargo and A. Ayalew, 2014].

The various components present in the effluent affect human beings, agriculture and livestock besides causing severe ailments to the tannery workers such as eye diseases, skin irritations, kidney failure and gastrointestinal problems. Tannery waste material also varies considerably in volume and concentration due to continuous operation and intermittent discharge [H. Dargo and A. Ayalew, 2014].

## 2.6 Pollutants in Tannery effluent

Usually tannery wastewater is characterized by strong color, high BOD, high COD, low pH and high dissolved salts. Disposal of these wastes into watercourses or onto land can cause irreversible damage to the environment in the vicinity <sup>(2).</sup>The main pollutants are sodium chloride, sodium sulphide/hydrosulphide, lime, chromium, preservatives, protein matter etc. Eighty to ninety percent tanneries use chromium (as Basic Chrome Sulphate) as a tanning agent. That include:

### 2.6.1 Solids:

Solid refer to matter suspended or dissolved in water or waste water <sup>(9)</sup>

the solids found in tannery effluent fall into several distinct categories that include:

**a. Suspended Solids:** The suspended solids component of an effluent is defined as the quantity of insoluble matter contained in the wastewater. These insoluble materials cause a variety of problems when discharged from a site; essentially, they are made up of solids with two different characteristics.

**B.** Solids with a Rapid Settling Rate (settleable solids): These solids originate from all stages of leather making; they comprise fine leather particles, residues from various chemical discharges and reagents from different waste liquors. Large volumes are generated during beam house processes.

**C. Semi-Colloidal Solids**: Semi-colloidal solids are very fine solids that, for all practical purposes, will not settle out from an effluent sample, even after being left to stand for a considerable period of time. Most of these solids are protein residues from the beam house operations – mainly liming processes; however, large quantities are also produced owing to poor uptake in vegetable tanning processes, another source being poor uptake during retanning. Semi-colloidal solids will not directly cause a sludge problem. They can be broken down over an extended period by bacterial digestion and they produce solids, which will eventually settle.

## 2.6.2 Oxygen Demand (Do)

Many components in effluents are broken down by bacterial action into more simple components. Oxygen is required for both the survival of these bacteria (aerobic bacteria) and the breakdown of the components. Depending on their composition, this breakdown can be quite rapid or may take a very long time. If effluent with a high oxygen demand is discharged directly into surface water, the sensitive nutrient balance maintained in the water becomes overloaded.

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### 2.6.3 Biochemical Oxygen Demand (BOD)

BOD is a measure of the oxygen requirements of bacteria under controlled conditions, to breakdown pollutants in the effluent in a period of 5 days. Many effluent components take longer time to break down. Some chemicals will only be partially broken down, while others may not be significantly affected. Typically, vegetable tanning wastes have a long breakdown period, often quoted as being up to 20 days. These longer digestion periods can apply to a variety of chemicals used in manufacturing leathers, including certain retanning agents, some synthetic fat liquors, dyes and residual proteins from hair solubilisation. This longer breakdown period means that the environmental impact is spread over a larger area as the waste water components are carried greater distances before broken down.

### 2.6.4 Chemical Oxygen Demand (COD)

COD is a measure of the oxygen required to oxidize the effluent sample wholly. It sets a value for the materials that would normally be digested in the BOD analysis, the longer term biodegradable products, as well as the chemicals that remain unaffected by bacterial activity. The results are always higher than those obtained through BOD5 analysis. As a rule of thumb, the ratio between COD: BOD is 2.5:1, although in untreated effluent samples variations may be as great as 2:1 or even 3:1. This depends on the chemicals used in the different leather making processes and their rate of biodegradability. The semi colloidal material that forms part of the suspended solids is also included in the BOD and COD determinations. Normally 1 mg/L suspended solids will generate a COD increase of approximately 1.5 mg/L.

#### 2.6.5 Nitrogen

Nitrogen is contained in several components in tannery effluent. Sometimes these sources have to be differentiated .that include:

**a. Total Kjeldahl Nitrogen (TKN):** Several components in tannery effluent contain nitrogen as part of their chemical structure. The most common chemicals are ammonia (from deliming materials) and the nitrogen contained in proteinaceous materials (from liming/unhairing operations).

**b.** Ammonium content as Nitrogen (N): These compounds are mostly the outcome of the deliming process, with comparatively small volumes being produced from liming and unhairing. This excludes the nitrogen component resulting from protein wastes.

## 2.6.6. Sulphide (S<sup>2</sup>-)

The sulphide content in tannery effluent results from the use of sodium sulphide, sodium hydrosulphide, and the breakdown of hair in the dehairing process.

### 2.6.7 Sulphates (SO<sub>4</sub>)

Sulphates are a component of tannery effluent, emanating from the use of sulphuric acid or products with a high (sodium) sulphate content. Many auxiliary chemicals contain sodium sulphate as a by-product of their manufacture. For example, chrome tanning powders contain high levels of sodium sulphate, as do many synthetic retanning agents. An additional source is created by removing the sulphide component from effluent by aeration since the oxidation process creates a whole range of substances, including sodium sulphate. These sulphates can be precipitated by calcium-containing compounds to form calcium sulphate which has a low level of solubility.

## 2.6.8 Chlorides (Cl<sup>3</sup>-)

Chloride is introduced into tannery effluents as sodium chloride usually on account of the large quantities of common salt used in hide and skin preservation or the pickling process. Being highly soluble and stable, they are unaffected by effluent treatment and nature, thus remaining as a burden on the environment. Considerable quantities of salt are produced by industry and levels can rapidly rise to the maximum level acceptable for drinking water.

### 2.6.9 Oils and grease

During leather manufacture, natural oils and grease are released from within the skin structure. If fat liquor exhaustion is poor, some fatty substances may be produced through inter-reaction when waste waters mingle. Floating grease and fatty particles agglomerate to form 'mats' which then bind other materials, thus causing a potential blockage problem especially in effluent treatment systems

#### 2.6.10. PH

Acceptable limits for the discharge of waste waters to both surface waters and sewers vary, ranging between from pH 5.5 to 10.0. Although stricter limits are often set, greater tolerance is shown towards higher pH since carbon dioxide from the atmosphere or from biological processes in healthy surface water systems tends to lower pH levels very effectively to neutral conditions. If the surface water pH shifts too far either way from the pH range of 6.5 - 7.5, sensitive fish and plant life are susceptible to loss [M. A. Mohamed, 2012].

### 2.6.11 Heavy metals

#### A/ Definition, classification, and sources in industrial waste water

There is no clear definition of what is heavy metal, but density is used in most cases to define heavy metals. Heavy metals are usually defined as having a specific density greater than 5 g / cm 3. The main threats to human health from heavy metals are associated with Exposure to lead, cadmium, mercury and arsenic. These

metals have been extensively studied and their effects on human health regularly reviewed by International bodies such as the WHO. Heavy metals have been used by Humans for thousands of years. Although several adverse health effects Of heavy metals have been known for a long time, exposure to heavy metals Continues, and is even increasing in some parts of the world, in particular in less developed countries, though emissions have declined in most developed countries over the last 100 years [L. Järup, 2003].

Living organisms require trace amount of heavy metals such as iron, cobalt ,copper ,manganese and zinc but this essential metals when increase from require limit can be harmful to the organisms .Non-essential heavy metals to organisms are well known toxic and carcinogenic agents such as lead, mercury, cadmium, chromium and arsenic. The main sources of heavy metals pollutants are industrial waste water from mining, metal processing, tanners, pharmaceutical, pesticides .organic chemical, rubber and plastics ...etc

#### B/ Regulatory limits and necessary of treatment

The maximum contaminant level (MCL) values as per EPA and the position in the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), 2005 list of priority chemicals of some of the toxic and heavy metals are summarized in Table 1 . The above limits are mandatory for all the water supply systems. But naturally occurring water (both surface and ground water) sometimes contain some of these heavy metals in 100 or 1000 times more in concentration than the prescribed MCL value. All water treatment facilities; therefore, are required to treat the heavy metals contaminated water to meet the regulatory requirements <sup>(11).</sup>

**Table 2-2:** Maximum concentration of heavy metals as per CERCLA list ofpriority chemicals 2005 and their regulatory limits [N. K. Srivastava and C. B.

Heavy metals	Maximum concentration limits
	(mg/l)
Arsenic (As)	0.01
Lead (Pb)	0.015
Mercury (Hg)	0.002
Cadmium (Cd)	0.005
Chromium (Cr (VI))	0.01
Zinc (Zn)	5
Manganese (Mn)	0.05
Copper (Cu)	1.3
Selenium (Se)	0.05
Silver (Ag)	0.05
Antimony (Sb)	0.006
Iron (fe)	0.3

Majumder].

## 2.6.12 Solvent

Solvents originate from degreasing and finishing operations. Solvents in effluents discharged to surface waters can form a microfilm on the water surface, thus inhibiting the uptake of oxygen. Solvents break down in a variety of ways; some inhibit bacterial activity and remain in the eco-system for extended periods of time [M. A. Mohamed, 2012].

#### 2.6.13 Chrome

#### a/ chrome chemistry

Chromium is a first series transition element from group VI B in the periodic table. In its elemental form, it is white, hard, lustrous, and brittle metal with a fairly high melting point (approximately 2000° C). It can exist in oxidation states ranging from -2 to + 6, but only the 0, +2, +3 and +6 forms are commonly encountered. The critical chemistry of chromium with respect to plant accumulation from the environment revolve around the reduction of Cr (VI) to Cr(III), the oxidation of Cr(III) to Cr(VI) and the relative stability of Cr(III) compounds once formed. In acid solution Cr2+ (chromous), Cr3+ (chromic), and Cr207.2 (dichromate) are representative and in basic solution Cr (OH)2, Cr02, Cr02.1 (chromite), and Cr02.2 (chromate) are representative. The chromous ion is rapidly oxidized to Cr (III) by air and slowly by H+. In its highest oxidation state chromium forms exclusively oxycompounds and all are potent oxidizing agents.

#### b/ Chromium in surface water

Naturally occurring levels of chromium in water can be very low, in the picogram per milliliter range. Chromium will be present in rivers as soluble and insoluble forms. Most of the soluble chromium is present as hexavalent chromium but this generally accounts for only a few percent of the total chromium. Chromium (III) will be present in solids suspended in the water as minerals, organics and occluded oxides. The actual concentration of chromium in water will depend on the source of the water and materials it passes through and carries with it. The importance of total chromium concentrations in water is not known. However, in many waters there is the possibility of oxidation of Cr (III) to Cr (VI). Very little is known about the behavior of soluble organic chromium in aqueous and biological systems and

there have been few studies on the importance of different phases in the transport of chromium in rivers Substances in natural water can inhibit the oxidation. Hexavalent chromium is reduced by ferrous iron, dissolved sulfide, and organic sulthydryl groups.

#### c/ Chromium in groundwater

Groundwater contamination by chromium is major problem in industrialized areas, particularly those that have large metal-plating industries. Other important industrial sources of chromium are wood treatment and tannery facilities, as well as chromium mining and milling operations. Typically, chromium-containing wastes have been disposed of by discharging them to surface impoundments or lagoons. Leakage from these lagoons into groundwater has been relatively common. Almost all reported incidences of chromium-related groundwater contamination are of industrial origin. Naturally occurring chromium also occurs at potentially harmful concentrations Groundwater contamination by chromium can be extensive in sand and gravel and fractured rock aquifers because groundwater velocities in these materials typically are between about 0.1 and 5m per day. At the other extreme, groundwater velocities in clayey materials tend to be low, approximately a few centimetres or less per year, so chromium-contaminated groundwater cannot extend far from the source. Saha (200 I) reported in his study that chromium from accumulated sludge and wastewater at Hazaribagh area penetrated into the soil. The accumulation was restricted primarily to the first 10 feet of soil and this was because the chromium present in the samples was mostly Cr (III) form. High level of chromium exceeding the drinking water standard of 0.05 mg/L were detected in the ground water samples. Saha (2001) concluded that chromium from Hazaribagh Tannery Industries had contaminated the ground water in and around Hazaribagh area. The mobility of chromium in groundwater depends

also on its solubility and its tendency to be adsorbed by soil or aquifer materials. These factors depend on the groundwater chemistry and the characteristics of soil or aquifer.

#### d/ Solubility of Chromium

There are no significant solubility constraints on the concentrations of Cr (VI) in groundwater. Solubility can, however, significantly limit the concentration of Cr (III) in groundwater at a pH above 4 or 5. The low solubility of the Cr (III) solid phases CrzO] is likely the major reason why Cr (III) generally makes up a small percentage of the total chromium concentration in natural or polluted groundwater and why it rarely occurs at concentrations above the drinking water standard of 0.05 mg/L. Chromium (III) tends to be essentially immobile in most groundwater because of its low solubility. Chromium (III) solution concentrations in equilibrium with CrzO) are less than 0.005 mg/L above a pH of 4, whereas Cr (III) solution concentrations in equilibrium with Cr (OH») vary from approximately 0.05 to 500 mglL between a pH of 5 and 9. Although the theoretical solubility of CrzO] is much lower than that of Cr (OH)], precipitate as Cr (OH)] in natural aqueous systems where waste has been introduced as Cr(VI) and subsequently been reduced to Cr(III). When Cr (VI) is transported by groundwater, it may be transformed to and precipitated as Cr (III) if the groundwater enters a low redox zone. Laboratory studies have shown that Cr (VI) can be reduced readily to Cr (III) in the presence of organic matter, especially at low pH. Chromium (III) generally is not transported to great distances by groundwater because of its low solubility. However, Cr(III) could be converted to the more soluble Cr(VI) if the redox state at a particular location occurs to change with time from reducing to oxidizing. Chromium (III) has been found to be oxidized by manganese under natural conditions.

#### e/ Chemical Speciation, Oxidation and Reduction

Chromium speciation is affected by Pe (redox) and pH conditions. Chromium (VI) predominates under oxidizing (high redox) conditions, whereas Cr (III) predominates under more reducing (low redox) conditions. Oxidizing conditions generally are found in shallow aquifers within a few meters of the water table, where there is a continual replenishment of oxygen from the atmosphere via the unsaturated zone. Oxygen in groundwater tends to be consumed by hydro chemical and biochemical oxidation reactions, usually involving organic matter. In shallow groundwater, this oxygen is replaced from the atmosphere. In deeper ground waters that are isolated from the atmosphere, no replenislnnent of oxygen occurs, and reducing conditions develop (Fig. 2.3). Chromium (VI) is extensively hydrolyzed in water. At total chromium concentrations below 500 mg/L (0.01 M), the dominant Cr (VI) species are the oxyanions HCr04- and CrOI Equilibrium between the two species is dependent on pH:

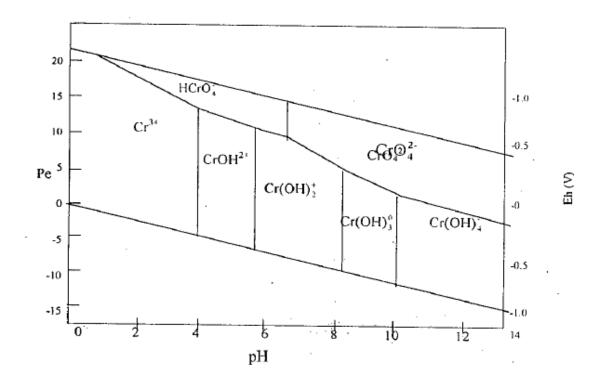
 $HCrO_4^{-} ---> CrO_4^{2-} + H^+$ 

At low pH, the concentration of H ions is high, so the reaction tends to the left, and HCr04- is the dominant species. At higher pH, where the H+ concentration is lower, the reaction tends to the right, and CrOl predominates. In natural groundwater, the pH is typically between 6 and 8, so the CrOl ion is the dominant species. At Cr (VI) concentrations above 500 mg/L, the Cr20/ ion predominates in acidic environments. However, Cr (VI) at concentrations on the order of 10 mg/L imparts a characteristic yellow color to water). Chromium (VI) does not commonly form complexes with inorganic or organic ligands .The dominant Cr (III) species occurring in groundwater also depend on pH.

$$Cr^{3}+ + H_{2}o <-> CrOH^{2+} + H^{+}$$

$$CrOH^{2}+ H_{2}O <-> Cr (OH) +_{2} + H^{+}$$
  
 $Cr (OH)^{+}_{2} + H_{2}O <-> Cr (OH)]_{3} + H^{+}$   
 $Cr (OH)_{3} + H_{2}O <-> Cr (OH)_{4} + H^{+}$ 

 $Cr (OH)_2$ +is the document species in natural groundwater with a pH between 6 and 8. CrOH<sub>2</sub>+ predominate in more acidic waters and Cr(OH)<sub>3</sub> and Cr (OH)<sub>4</sub> predominate in more alkaline waters. Chromium (III) complexes with many organic ligands, as well as fluoride, ammonia, cyanide, thiocyanate, oxalate, and sulfate. Reduction strategies for Cr(VI) in soils are based on the concept that Cr(III) has negligible toxicity and minimal mobility compared with Cr(VI) and, therefore, reduction of Cr(VI) to Cr(III) is a means of eliminating the hazard associated with Cr contamination in a soil without changing its total Cr concentration. Successful strategies for effecting such remediation must satisfy three criteria: (1) newly reduced Cr(III) is in a form that is inert to re-oxidation, (2) extraneous or objectionable byproducts of the Cr(VI) reduction reaction are not released (e.g., nitrate, Fe(III) oxide crusts, or partially oxidized Sulphur-containing compounds), and (3) oxidation-reduction and acidity conditions of the soil are controlled so that Cr(III), other metals or soil pollutants are not solubilized. In addition, marked changes in these conditions could inhibit the desired Cr(VI) reduction reaction. Element Fe (e.g., steel wool) reduces Cr (VI) to Cr (III) in chromates processing residue-enriched soils and other aqueous environments, and in the process, alkalinity is generated. The Fe(III) and Cr(III) formed by the redox reaction may create a mixed oxide with low solubility, thereby minimizing the chances for re-oxidation of Cr(III). In contrast, reduction of Cr (VI) coupled to oxidation of Fe(II) compounds may generate net acidity, and the soil pH may decrease markedly, depending on the pH buffer capacity to the soil. Similar mixed Cr(III) Fe(III) oxides may form, however. The reduction of Cr(VI) by organic compounds (e.g., hydroquinone) will also generate alkalinity, and newly formed Cr(III) maybe Complexed with organic materials, such as humic acids in soils. Such complexation in insoluble forms will inhibit reoxidation if Cr (III) is bound in insoluble organic complexes (e.g., with humic acids).



**Figure 2-4:** Areas of dominance of dissolved chromium species at equilibrium in the system at 2SoC [S. Obaidullah and A. L. Mahmood, 2008].

In contrast, solubilization of Cr (III) by orgame acids may increase oxidation of Cr(lll), depending on the form of Cr, pH, and the organic acid involved. The most efficacious methods for remediation Cr(VI)-contaminated soils will depend on native soil pH, the presence of natural reducing agents, forms of Cr(VI) present (e.g., their solubility), the pH buffer capacity of the soil, and the ease with which the reducing agents may be incorporated into depths soil where Cr(VI) is found.

#### f/ Adsorption and Precipitation

Soil pH determines both the speciation of Cr(VI) and the change characteristic of the colloidal surface with which it reacts. Above pH 6.4,  $HCrO_4^-$  dissociates to  $CrO_4^{-2}$  as the dominant form of Cr(VI) in dilute aqueous systems. Divalent  $CrO_4^{-2}$ may be adsorbed in similar fashion to  $SO_4^{-2}$  and  $HPO_4^{-2}$ , forming binuclearbridged complexes on goethite or on aluminum oxides and other soil colloids with positively charged surfaces. Chromate also may be absorbed by ligand exchange on Fe(III) and Al(III) oxides . Depending on the colloid,  $HCrO_4$  may be similar to  $H_2PO_4^{--}$  and be tightly held in soils, or it may be similar to  $HCO_3^{--}$ ,  $CL^-$  and  $NO_3$ and remain soluble. Soil pH also affects the quantities of positive and negative charge on soil colloids, especially on organic matter and on Fe(III), AI(III), and Mn(III, IV) oxides. Binding of Cr(VI) species in soils will depend on soil mineralogy and on the relation of soil pH to the pH of zero point of charge of the colloids involved.

#### g/ Toxically of chromium

Chromium is not acutely toxic to humans. This is due to the high stability of natural chromium complexes in abiotic matrices. In addition, the hard acid nature of chromium imparts strong affinity for oxygen donors rather than sulfur donors present in bio-molecules. However, Cr (+6) is more toxic than Cr (+3) because of its high rate of adsorption through intestinal tracts. In the natural environment, Cr(+6) is likely to be reduced to Cr (+3), thereby reducing the toxic impact of chromium discharges. Chromium and dichromate were frame shift mutagens III the Salmonella plate incorporation test, through trivalent chromium did not cause an increase in reversion frequency. It appears, based on experimental evidence, that hexavalent chromium also has mutagenic properties. Although the case for

trivalent chromium is not as strong, its mutagenicity must be considered a possibility. Epidemiological studies have shown a positive relationship between occupational exposure to chromates and cancer incidence. Risk of lung cancer appears greatest among ferrochromium, chromate and chrome pigment workers. Slightly soluble hexavalent chromium salts, specifically calcium chromate, are the most potent carcinogens. These compounds have induced high levels of chromosomal aberrations in cultures of mammalian cells.

#### h/ Health Aspects of Chromium:

Chromium appears to be necessary for glucose and lipid metabolism and for utilization of amino acids in several systems. It also appears to be important in the prevention of mild diabetes and arteriosclerosis in humans. The harmful effects of waterborne chromium in man are associated with hexavalent chromium; trivalent chromium, which is regarded as a form of chromium essential to man, is considered practically non-toxic and 110 local or systemic effects appear to have been reported. People living in areas of the world where arteriosclerosis is virtually absent tend to have higher chromium levels in tissues than people from areas where the disease is endemic. Hexavalent chromium at 10 mg/kg of body weight will result in liver cero sis, nephritis, and death in man; lower doses will cause irritation of the gastrointestinal mucosa. Hexavalent chromium has been implicated as the cause of digestive tract cancers in man, and there is firm evidence that there is an increased risk of lung cancer for workers who are exposed to high levels of chromium. Exposure to a mixture of chromium (VI) compounds of different solubilities (astound in the chromate production industry) carries the greatest risk of human beings

# 2.7 Impact of tannery effluent on environment and health:

# 2.7.1 Effects on Air Quality

Biological decomposition of organic materials as well as sulphide emissions from wastewater, are responsible for the characteristics objectionable odours from the tanneries and their wastes. The following are important sources of odours:

- Sulphide emissions from de-hair and waste treatment.
- Ammonia emissions from deliming.
- fleshing.

#### 2.7.2 Effects on Human Health:

A study about the prevailing health problems of the workers of tannery industries found that, continuous handling of chemicals cause cumulative effect in the human body. that clinical manifestations similar to chromium toxicity like abdominal discomfort/gastritis, skin, ulcer, dermatitis, nausea, ulcer/loss a of smell, erosion and discoloration of teeth and asthma were found among the people who worked in the tannery industry and also those who are living in and around the tannery industrial area for more than 10 years [S. Obaidullah and A. L. Mahmood, 2008].

# 2.8 Wastewater production

Table 2-3 provides an overview on water consumption in individual processing operations during the tanning process, Depending on the type of applied technology (conventional or advanced) the water consumption varies extremely. Technologies that can be regarded as advanced in comparison to conventional methods involve processes usually termed low-waste or cleaner technologies (high

exhaustion, chrome fixing), mainly in dry regions, where water supply is limited, this factor plays an important role.

Operation	Discharge (m <sup>3</sup> /t raw hide)			
	С	Α		
Soaking	7-9	2.0		
Liming	9-15	4.5		
Deliming ,bating	7-11	2.0		
Tanning	3-5	0.5		
Post tanning	7-13	3.0		
Finishing	1-3	0		
Total	34-56	12		

 Table 2-3: Water consumption in individual processing operations

(C-conventional technology, A-advanced technology)[N. Technologien, 2002].

In addition to the water required for individual processing operations, a certain amount of water is used in pasting/vacuum dryers, for cleaning, or sanitary and similar purposes. The minimum volume required is 2-3 m3/t raw hide under conditions of very good housekeeping [N. Technologien, 2002]

**Table 2-4:** Summary of pollution loads discharged in effluents from individualprocessing operations (C-conventional technology, A-advanced technology) [N.Technologien, 2002].

Operat         Technol         Pollution load (kg/t raw hide)										
ion	ogy	SS	COD	BOD	Cr	S <sup>2-</sup>	NH3-N	TKN	CL-	<b>SO</b> <sub>4</sub> <sup>2-</sup>
				5						
Soaking	С	11-17	22-33	7-11	-	-	0.1-0.2	1-2	85-	1-2
									113	
	А	11-17	20-25	7-9	-	-	0.1-0.2	1-2	5-10	1-2
Liming	С	53-97	79-	28-45	-	3.9-	0.4-0.5	6-8	5-15	1-2
			122			8.7				
	А	14-26	46-65	16-24	-	0.4-	0.1-0.2	3-4	1-2	1-2
						0.7				
Delimin	С	8-12	13-20	5-9	-	0.1-	2.6-3.9	3-5	2-4	10-
g,						0.3				26
bating	А	8-12	13-20	5-9	-	0-0.1	0.2-0.4	0.6-	1-2	1-2
								1.5		
Tannin	C	5-10	7-11	2-4	2-5	-	0.6-0.9	0.6-	40-60	30-
g								0.9		55
	А	1-2	7-11	2-4	0.05	-	0.1-0.2	0.1-	20-35	10-
					.0.1			0.2		22
Post	С	6-11	24-40	8-15	1-2	-	0.3-0.5	1-2	5-10	10-
tanning										25
	А	1-2	10-12	3-5	0.1-	-	0.1-0.2	0.2-	3-6	4-9
					0.4			0.5		
Finishin	C	0-2	0-5	0-2	-	-	-	-	-	-
g	А	0-2	0	0	-	-	-	-	-	-
Total	С	83-	145-	50-86	3-7	4-9	4-6	12-18	137-	52-
		149	231						202	110
	А	35-61	96-	33-51	0.15	0.4-	0.6-1.2	5-8	30-55	17-
			133		-0.5	0.8				37

# 2.9 Wastewater treatment

The degree of treatment required can be determined by comparing the influent wastewater characteristics to the required effluent characteristics, adhering to the regulations. Number of different treatment alternatives can be developed to achieve the treated wastewater quality.

# 2.9.1 Classification and Application of Wastewater Treatment Methods:-

The individual treatment methods are usually classified as:

- Physical unit operations (Mechanical or primary treatment).
- Biological unit processes (secondary treatment).
- Chemical unit processes [M. & Eddy, 2003].

## 2.9.2 Tannery Wastewater treatment methods

Tanning industry is one of the oldest industries of the world and the problem of treatment and disposal of these wastes is probably as old as the industry itself <sup>(12)</sup>. Before turning to treatment itself, it is important to bear in mind the following:

• The design of an effluent treatment plant (ETP) is always tailored to the requirements of a specific site; thus, there are no two identical ETPs.

• Pollutants contained in effluent cannot disappear; they are only converted into something which is environmentally more acceptable or easier to dispose of (sludge).

• Somewhat paradoxically, the obvious is often overlooked: the same amount of pollutants at lower water consumption means lower hydraulic load (volume) but higher concentration – not always easy to treat.

• It is important for a tanner to understand the relation between the leather technologies applied and wastewater treatment in order to reduce the overall cost of treatment.

Wastewater treatment is a multi-stage process to purify wastewater before it enters a body of natural water, or it is applied to the land, or it is reused. The goal is to reduce or remove organic matter, solids, nutrients, Cr and other pollutants since each receiving body of water can only receive certain amounts of pollutants without suffering degradation. Therefore, each effluent treatment plant must adhere to discharge standards limits usually promulgated by the relevant environmental authority as allowable levels of pollutants, for practical reasons expressed as BOD5, COD, suspended solids (SS), Cr, total dissolved solids (TDS) and others. The three main categories of tannery wastewater, each one having very distinctive characteristics, are:

• Effluents emanating from the beam-house – liming, deliming/bating, water from fleshing and splitting machines; they contain sulphides, their pH is high, but they are chrome-free.

• Effluents emanating from the tanyard (tanning and re-tanning, sammying) – high Cr content, acidic.

• Soaking and other general effluents, mainly from post-tanning operations (fatliquoring, dyeing) – low Cr content.

Very arbitrarily and not quite consistently we speak of the following main phases of treatment:

**1**/ **Preliminary treatment** :Typically, in the case of common effluent treatment plants (CETPs) servicing tannery clusters often found in developing countries, it is

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essential to have pre-treatment units installed in individual tanneries. Their role is to remove large particles, sand/grit and grease, but also to significantly reduce the content of chrome and sulphides before the effluent is discharged into the collection network.

#### 2/ Physical-chemical treatment (primary)

The objective here is the removal of settleable organic and inorganic solids by sedimentation, and the removal of materials that will float (scum) by skimming. Approximately 25-50% of the incoming biochemical oxygen demand (BOD5), 50-70% of total suspended solids (SS), and 65% of the oil and grease are removed during primary treatment. The effluent and sludge from primary sedimentation are referred to as primary effluent and sludge.

## **3/Biological treatment (secondary)**

In most cases, secondary treatment follows primary treatment, its goal being the removal of biodegradable dissolved and colloidal organic matter using aerobic biological treatment processes. Aerobic biological treatment is carried out in the presence of oxygen by aerobic micro-organisms (principally bacteria) that metabolize the organic matter in the wastewater, thereby producing more micro-organisms and inorganic end products (principally CO2, NH3, and H2O). Several aerobic biological processes are used for secondary. Treatment and the differences among them have to do primarily with the manner in which oxygen is supplied to the micro-organisms and with the rate at which organisms metabolize the organic matter.

**4/ Advanced (tertiary) treatment:** Tertiary or advanced wastewater treatment is employed to reduce residual COD load and/or when specific wastewater constituents are not removed by previous treatment stages.

#### 5/ Sludge handling and disposal

Effluent treatment plants produce treated, "cleaned" effluent and sludge because inherently the primary aim of wastewater treatment is the removal of solids and some potentially hazardous substances from the wastewater. Furthermore, biologically degradable organic substances are converted into bacterial cells, and the latter are removed from the wastewater <sup>(13)</sup>. Tanneries wastewater effluent is treated in many different ways. There are situations in which an individual tannery applies all the below-described wastewater treatment steps on site. In other situations an individual tannery may apply (on site) only pre-treatment or a part pre-treatment or no treatment at all, sending the effluent to a centralized effluent treatment plant. Nevertheless, a treatment is necessary due to the wide range of toxic effects on the environment caused by untreated tannery effluents and sludges. The following treatment steps are necessary and will be described in more detail afterwards:

- Mechanical treatment
- Effluent treatment
- Post-purification, sedimentation and sludge handling.

## 2.9.3 Primary treatment (mechanical and chemical treatment)

## 1/ Objectives:

• To remove the coarse material normally present in the raw wastewater that could clog or block pumps, pipes and possibly sewer lines.

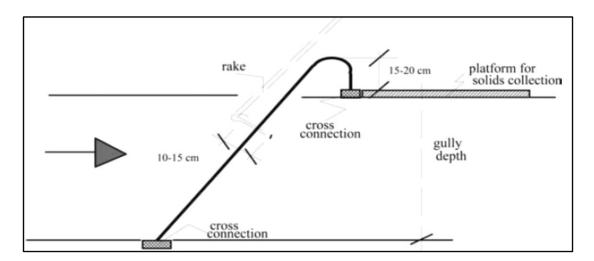
• To mix and balance well different tannery streams and thus produce homogenized "raw material" that can be treated in a consistent manner.

• To adjust pH and removal toxic substances (sulphides) and avoid shock loads that can negatively affect the rather sensitive biological treatment.

• To significantly decrease the BOD/COD load and thus simplify the biological treatment phase and reduce its cost. To summarize, the purpose is to eliminate the coarse matter, remove almost completely Cr and sulphides, remove the major part of suspended solids, and considerably reduce the BOD and COD content.

The basic steps in this treatment as follows:

# 1/ Screening

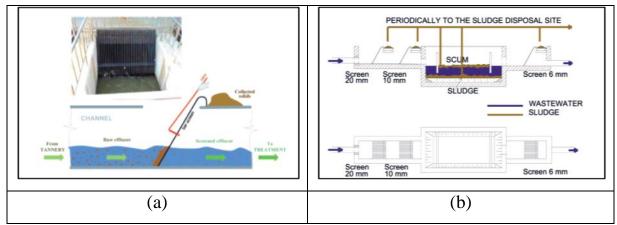


# A/ Bar screening, removal of larger solids

Figure (2-5): Rough bar screen, side view [A. Itodo1, 2018].

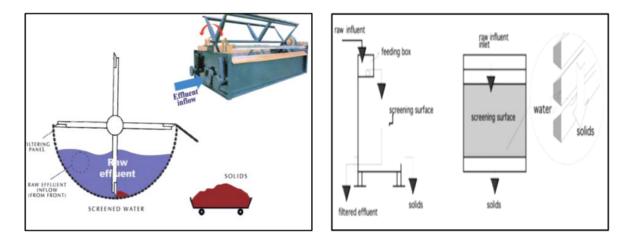
# B/ Removal of grit and floating matter

A simple, non-aerated grit-and-floating-matter removal chamber is usually placed in a horizontal gravity channel immediately after the rough screen.



**Figure (2-6):** (a) Rough bar screen, operation principle. (b) Simple, non-aerated grit-and-floating-matter removal chamber [A. Itodo1, 2018].

# C/ Self-cleaning screens

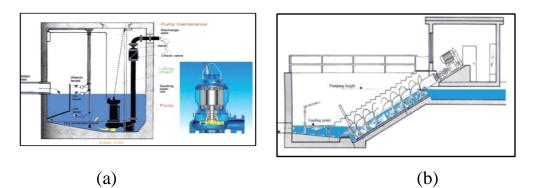


(a) (b) **Figure (2-7):** (a) Self-cleaning, rotary-brush screen, Park wood type (b) Selfcleaning

Screen, hydro sieve type [A. Itodo1, 2018].

# 2/ Pumping/lifting

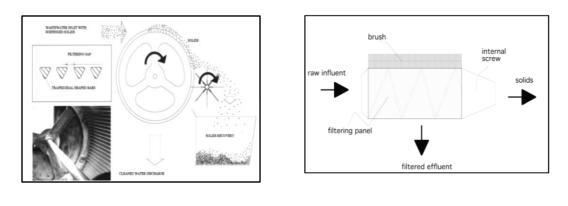
It is not possible to transfer effluents throughout the ETP by gravity only; at least one, often more pumping/lifting stations are needed, the first typically located before the rotary screen. Depending on specific Requirements (capacity/flow), different types of pumps are used. For medium-scale ETPs, submersible pumps are generally used for this purpose, for large-volume ones, screw (Archimedes) pumps are preferred. The scheme of submersible pump positioning (usually with a standby pump) is shown below:



**Figure (2-8): (**a) Submersible pump (b) Schematic view of an Archimedes-type lifting pump [A. Itodo1, 2018]

# 3/ Fine screening

Fine screening should drastically reduce the amount of fine suspended solids. Figure (2-10) below show rotary-drum screens with outer and inner flow:





(b)

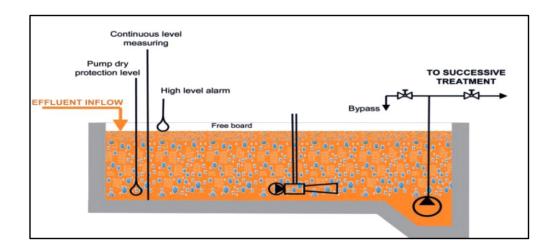
**Figure (2-9):** (a) Rotary-drum (Konica) screen, outer flow (b) Rotary-drum fine screen, inner flow [A. Itodo1, 2018].

## 4/ Equalization – homogenization – sulphide oxidation

The main aims here are:

- Homogenization of the effluent (quantity and quality); and
- Sulphide elimination, mostly by catalytic oxidation.

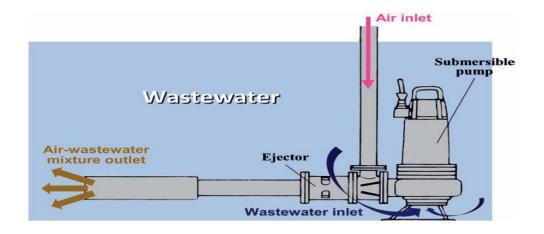
It is very important to keep all particulate matters in suspension, i.e., to avoid settling of solids. This is achieved by using mixing-cum-aeration devices such as diffused-air systems (preferred), Venturi ejectors, and fixed or floating aerators (lately avoided due to lower efficiency and the problem of aerosols). In practice, to play it safe, the volume of the equalization tank corresponds to the total daily effluent discharge.



**Figure (2-10):** Schematic view of equalization, homogenization tank [A. Itodo1, 2018].

Approximately 1 kg of O2 is needed to oxidize 1 kg of S2- to thiosulphate, whereas the oxygen transfer efficiency is about 1.5 kg O2/kWh (simplified approximation: 1 kg S<sup>2-</sup> = 1 kg O<sub>2</sub> = 1kWh). Again, in practice, attention is focused on the energy required to keep the solids in suspension (some 50 W/m3), which is

then sufficient for sulphide oxidation; the amount of catalyst, MnSO4  $\cdot$  4 H2O, industrial purity, is about 20 g per cubic meter of tank capacity. Whichever the mixing/aeration system chosen, it is necessary to be possible to remove the mixing device without stopping the treatment process. The inlet and the outlet of the equalization tank should be as far away from each other as possible to allow proper mixing (and no short-circuiting).



**Figure (2-11):** Venturi-type ejector often installed for mixing and aeration in the homogenization tank [A. Itodo1, 2018].

A typical equalization tank will have transfer pumps for equalized effluent. The capacity of the pumps is based on tank capacity, transfer time and head. One pump of cast iron with inside parts of stainless steel and one stand-by pump are sufficient unless effluent volume is very high (say 1,500 m3/d or more). The pumping line(s) are also a good place to set an electro-magnetic flow meter.

#### **2.9.4** Chemical treatment (coagulation, flocculation)

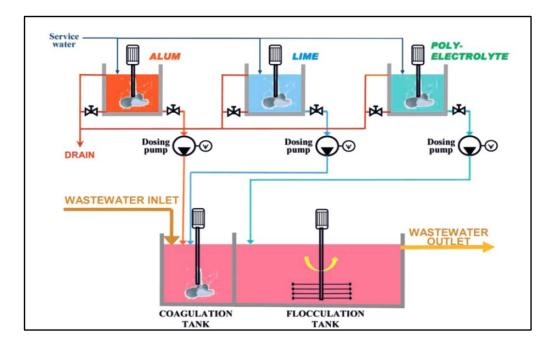
Chemicals are added in order to improve and accelerate the settling of suspended solids, especially of fine and colloidal matter. In wastewater treatment operations, the processes of coagulation and flocculation are employed to separate suspended solids from water. These terms are often used interchangeably, or the single term – be it "coagulation" or "flocculation" – is used to describe both; sometimes "flocculation" is understood as the second stage of "coagulation". In fact, they are two distinct processes usually carried out in sequence as a combination of physical and chemical procedures. Finely dispersed solids (colloids) suspended in wastewater are stabilized by negative electric charges on their surfaces, causing them to repel each other. Since this prevents these charged particles from colliding to form larger masses, called flocs, they do not settle. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge (zeta potential) of the colloids. As a result, the particles collide to form larger particles (flocs). Rapid mixing is required to disperse the coagulant throughout the liquid. Care must be taken not to overdose the coagulants as this can cause a complete charge reversal and thus re-stabilize the colloid complex.

Flocculation is the action of polymers to form bridges between flocs and bind particles into large agglomerates or clumps. In this process it is essential that the flocculating agent be added by slow and gentle mixing to allow for contact between the small flocs and to agglomerate them into larger particles. The newly formed agglomerated particles are quite fragile and can be broken apart by shear forces during mixing. Care must also be taken not to overdose the polymer as doing so will cause settling/clarification problems. Once suspended particles are flocculated into larger particles, they can usually be removed from the liquid by sedimentation, filtration, straining or floatation. The flocculation reaction not only increases the size of floc particles in order to settle them faster, but also affects the physical nature of flocs making them less gelatinous and thereby easier to dewater. The inorganic coagulants are compounds that break colloidal suspensions and help

floc forming. The most frequently used coagulants in tannery effluent treatment are:

- Alum: industrial aluminium sulphate Al<sub>2</sub>(SO4)<sub>3</sub> · 18H<sub>2</sub>O
- Iron sulphate: industrial  $FeSO_4 \cdot 7H_2O$
- Iron chloride: industrial  $FeCl_3 \cdot 6H_2O$
- Lime: industrial calcium hydroxide Ca(OH)<sub>2</sub>

Coagulant aids – flocculants – are water-soluble organic (anionic) polyelectrolytes that support agglomeration of colloidal and very fine suspended matter thus enhancing the impact of coagulation.



**Figure (2-12):** Schematic view of the coagulation and flocculation system [A. Itodo1, 2018].

For optimal results, appropriate dosing is essential; it should not be overlooked that, in addition to costs, these chemicals also influence not only pH (acidification)

but also TDS. On-the-spot investigation - jar tests using either sophisticated apparatus or simple tools (shown below) - is a must.

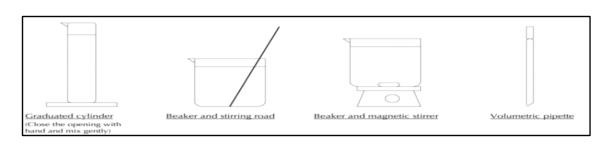


Figure (2-13): Some simple laboratory utensils [A. Itodo1, 2018].

Chemicals (pre)dissolved in small tanks with stirrers are usually added in the flash mixers – special "boxes" for rapid mixing placed before the primary settling tank. The contact time in the flash mixer is about 5 minutes for coagulation and some 20 minutes for flocculation; in the latter case, slow mixing to avoid floc shearing is essential. Hence, for example, if the capacity of the equalized effluent transfer pump is 60 m<sup>3</sup>/h, the usable volume of the coagulation and flocculation tank respectively should be  $60 \cdot 1/12 = 5$  m<sup>3</sup> and  $60 \cdot 1/3 = 20$  m<sup>3</sup>.

Ideally, two tanks should be available for the preparation of each chemical – one for solution preparation, the other for feeding the solution to the effluent. By having two tanks, levels of chemical dosing can be better controlled. The feeding of chemicals is done by dosing pumps.



(a) (b)
 Figure (2-14): (a) Coagulant/flocculent dosing station (b) "Flocs" after coagulation-flocculation [A. Itodo1, 2018].

# 2.9.5 Settling – primary sedimentation

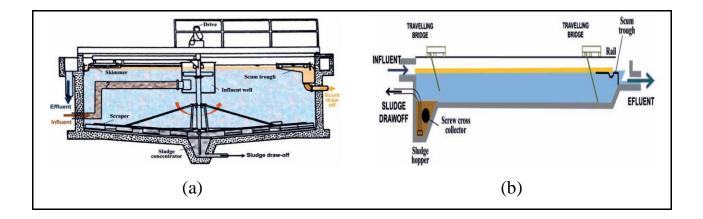
The main objective at this stage is the removal of suspended solids; however, various constituents such as fats, waxes, mineral oils, floating non-fatty materials, etc. ("grease"), not already removed in the grit-and oil chamber (usually positioned between screening and equalization) are also separated here. Primary settling tanks (clarifiers) are either circular (more commonly used) or rectangular with continuous grease (scum) removal at the top and sludge removal at the bottom. The key design parameters are:

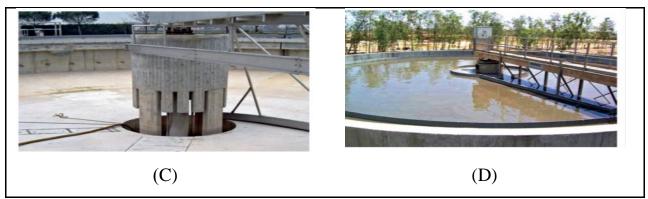
• Detention time – usually 1 - 2 hours (vertical clarifiers of the Dortmund type);

• Surface hydraulic loading, expressed in m3/m2 of tank surface per hour or m/h, typically 1 - 2  $m^3/m^2$  per hour;

• surface solids rate, expressed in kg/m2 and indicating the quantity of SS crossing the surface area of the tank over a certain time span (hour, day).

The surface solids rate is most frequently used in the design of sludge thickeners but, due to the quantity (4-6 g/l) and flocculent nature of tannery effluent solids, it is useful in controlling the primary sedimentation as well. Circular tanks are generally preferred as recirculation is easier. A mechanical device (scraper) is necessary in larger settling tanks.

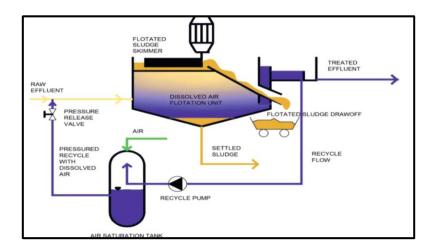




**Figure (2-15):** (a) Cross section of a typical circular sedimentation tank (b) Cross section of a rectangular sedimentation tank with travelling bridge shown in two positions

(C) Sedimentation tank (empty) (D) Sedimentation tank in operation [A. Itodo1, 2018].

In some cases, mainly due to space shortage, solids are removed by flotation, usually by the dissolved-air flotation (DAF) system.



**Figure (2-16):** Schematic view of a dissolved-air flotation (DAF) unit [A. Itodo1, 2018].

# 2.9.6 Sludge dewatering

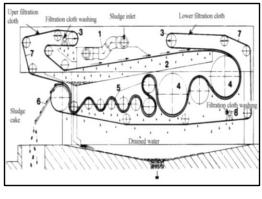
The sludge drawn from the bottom of the tank is in the form of slurry with a drysolid (DS) content of only 2-4%. For its evacuation, special pumps – usually of the Mohno type – are used. For further handling and disposal of sludge, it is necessary to reduce drastically the water content. This is usually achieved by:

(i) Thickening in sludge thickeners (very much like circular clarifiers).

(ii) Mechanical dewatering in filter presses, belt-filter presses or decanters (centrifuges).

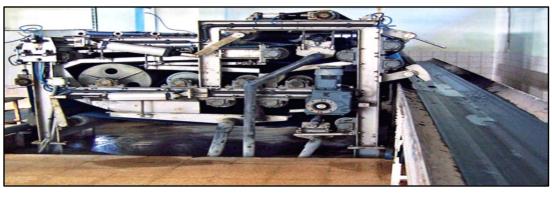
(iii) Natural drying in sludge-drying beds. In addition to power and chemical requirements, the key parameter for equipment selection is the achievable dry matter content in the dewatered sludge.







(b)



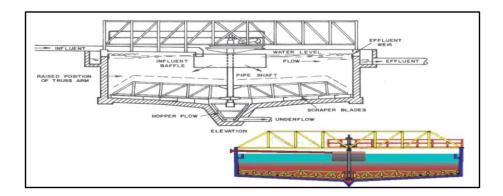
<sup>(</sup>C)

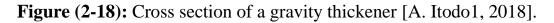
Figure (2-17): (a) Recessed-plate filter press with container for dewatered sludge

(b) Cross section of a belt-type press for sludge dewatering (c) Belt press with transporter for dewatered sludge [A. Itodo1, 2018].

# 2.9.7 Sludge thickener

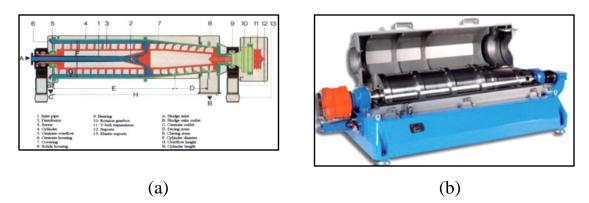
The construction of the sludge thickener is in practice identical with that of the sedimentator although in some cases the Dortmund type with self-desludging slopes is also used.





# 2.9.8 Centrifuge

By increasing dewatering level, improving wear and tear resistance (especially in the case of sludge containing fine sand) as well as by lowering irritating noise, centrifuges have succeeded in conquering a lot of ground in the treatment of tannery effluents.



**Figure (2-19):** (a) Cross section of a sludge dewatering centrifuge (b) Sludge dewatering centrifuge (the lid is up for a better view [A. Itodo1, 2018].

## 2.9.9 Sludge-drying beds

Easily constructed with locally available materials, drying beds were perceived as the best solution for tanneries in hot-climate developing countries. However, they require a lot of area, the output during rainy season's drops considerably, there is the problem of malodour, they are not easy to clean and made ready for the next batch, etc. For these reasons, sludge-drying beds are still used mainly by small tanneries not close to residential areas and/or as fall-back units used during breakdowns of mechanical dewatering equipment.

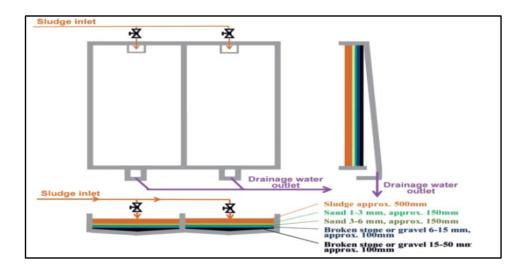


Figure (2-20): Schematic views of sludge-drying beds [A. Itodo1, 2018].

The products of primary treatment are:

(i) Primary treated effluent – overflow from the primary settling tank

With only residual amounts of chrome and sulphide and significantly reduced BOD, COD and SS content; and

(ii) Dewatered sludge with approximately 40% DS; its chrome content depends on the type and efficiency of the chrome management system applied. For the fortunate tanneries coupled to the sewage system, on-site treatment ends here – the biological treatment takes place together with urban wastewater in large WWWs. Usually, industrial effluents are only a small fraction of the total volume so that the salinity (TDS) they bring along does not represent a problem.

**Table (2-5):** Purification efficiency of treatment stages referred to raw effluent [A.Itodo1, 2018].

Parameter	Physical-chemical (primary)		Biological			
	Reduction%	Approx. value	Reduction%	Approx.		
		mg/l		value mg/l		
SS	80-90	300-600	95-98	20-50		
BOD	50-65	750-1500	97-99	20-30		
COD	50-65	1500-3000	87-93	250-400		
ТКН	40-50	250-300	60	100-200		
Cr	92-97	5-10	99-99.5	<1		
S <sup>-2</sup>	80-90	10-20	10-20 99-99.5			
TDS ,mainly	No reduction					
Cl <sup>-</sup> and SO <sup>-2</sup>						

•Approximately at the load level of 0.30 kg BOD5/kg MLSS, oxygen requirement of 2.0 kg O2/kg BOD5 and MLSS 3300 g/m3.

# 2.10 Secondary treatment (biological treatment and secondary sedimentation)

## 1/ Objective and basic principles

The main objective at this stage is to further reduce the amount of organic (expressed as BOD and COD) and other substances still present in the effluent after the primary treatment and there by satisfy the standards/limits for discharge into surface waters (rivers, lakes).

The biological treatment duplicates processes that take place in nature, but under controlled conditions and, especially, at a highly accelerated pace; however, the efficiency of this treatment largely depends on the biodegradability of the polluting substrate, i.e., its inherent capacity to decompose by biological processes. The remaining suspended and colloidal solids are removed by flocculation and adsorption. While biological treatment may be aerobic, facultative or anaerobic (or some combination thereof), in practice, almost only aerobic systems are used; exceptionally, in countries with a hot climate and where a lot of land is available, facultative (preferably aerated/facultative) lagoons are also used. Due to the inherent characteristics of tannery effluents, primarily their sulphide/sulphate content, in practice, anaerobic treatment is used only in sludge digestion. Among many variations of the aerobic process, the most widely used method is (complete-mix) activated sludge treatment with extended aeration; despite some very interesting features, membrane bioreactors (MBRs) have not made significant inroads in the tanning sector.

The activated sludge process is an aerobic, biological process, which uses the metabolism of microorganisms to remove substances causing oxygen demand. The

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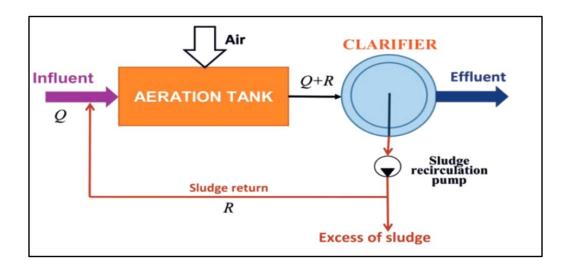
qualitative biochemical reaction taking place in the organic matter stabilization process can be summarized in the following manner:

# **Inert matter + organic matter + oxygen + nutrients + micro-organisms**

# -> New micro-organisms + $CO^2$ + $H_2O$ + additional inert matter

Simply said, we stimulate micro-organisms to convert (eat and digest) harmful, oxygen-demanding organic compounds into an environmentally more acceptable form (micro-organisms) and low energy, stable compounds like water and carbon dioxide.

The microbial community that does that job comprises various species of bacteria, fungi, protozoa, sometimes rotifers (multicellular animals only found in very stable activated sludge with long retention times), even nematodes, the composition of the population depending on a plethora of factors.



**Figure (2-21):** A simplified flow diagram of the activated sludge process [A. Itodo1, 2018].

Generally, the biological stage is the most complex part of the overall effluent treatment process, with highest investment and operational costs, its day-to-day running requiring considerable skills and experience [A. Itodo1, 2018].

#### 2.10.1 Aerobic Treatment

Aerobic microorganisms use organic carbon in the effluent and convert it to biomass and carbon dioxide. A large amount of sludge is generated along with high energy consumption. Aerobic treatment of tannery wastewater reduces chemical oxygen demand (COD) by 60-80% and biological oxygen demand (BOD) reduction is 95%, when combined with physicochemical pretreatment.

In a combined biochemical oxidation and chemical coronation step, chemical oxygen demand (COD), total nitrogen (TN) and total suspended solids (TSS) removals of 96%, 92% and 98%, respectively were obtained. Ozonisation step was integrated with sequencing batch bio film reactor. Ozonisation partially oxidizes there fractory compounds present in tannery wastewater and increases their bio degradability. Sludge production was 0.1 kg VSS/ kg COD removed, which is lower than the value reported in the literature for conventional biological systems. Aerobic treatment followed by chemical ozonisation and again aerobic treatment further increases the biodegrability of refractory compounds.

A combination of electrochemical and biological treatment can also be used to eliminate ammonia and avoid implementation of biological nitrification. Respirometry combined with sequencing batch reactor is an effective method for the removal of COD in tannery effluent. At 12h sequencing batch reactor cycle with a loading rate of 1.9-2.1 kg/m3 day, removals of COD, TKN and NH3-N were 80-82%, 78-80% and 83-99%, respectively. The removal efficiencies were much higher than conventional aerobic systems [H. Dargo and A. Ayalew, 2014].

# 2.10.2 Aeration devices

Water (effluent) aeration is important business that employs a wide range of equipment. In addition to cost, reliability, etc., the key criterion is the amount of air (oxygen) transfer per kW installed. Here is one – rather arbitrary – classification:

a. Surface aerators: include:

-Radial flow, low speed, 20-60 rpm.

-Axial flow, high speed, 300-1200 rpm.

-Brush rotor (oxidation ditch).

b. Submerged turbines.

c. Diffusers: include:

-Bubblers – porous and non-porous diffusers.

-Tubular.

-Jets (developed from Venturi ejectors).

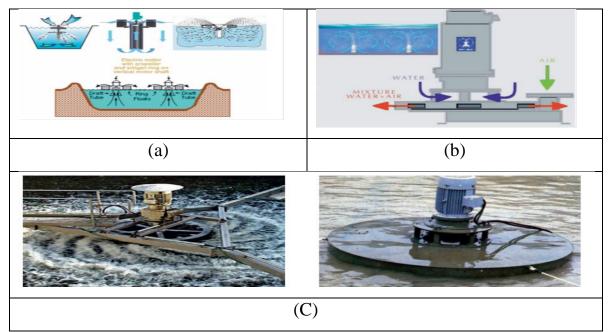


Figure (2-22): (a) Surface (floating) aerators (b) Forced-air, submersed turbine aerator (C) Surface aerators [A. Itodo1, 2018].



Figure (2-23): Bottom air diffuser grid with one section and fine-bubble dome diffuser [A. Itodo1, 2018].

# 2.10.3 Aeration basins, oxidation ditch

The possibly best biological treatment of tannery effluents is the oxidation ditch (OD) and its various derivatives – a circular aeration basin (racetrack-shaped), with rotary-brush or vertical-rotor (carrousel) aerators that extend across the width of the ditch. In addition to its simple construction and easy maintenance, the main advantage of the OD is its resilience to variations in flow, pollution load, including shock loads. It is even possible to combine several ovals and maintain different aeration regimes suitable for nitrification and denitrification.



**Figure (2-24):** Oxidation ditch in operation Oxidation ditch in operation [A. Itodo1, 2018].

#### 2.10.4 Secondary sedimentator

Their design is very similar to those of primary sedimentator, but the operational conditions are different. Also, the (excess – wastage) sludge evacuated at the tank bottom is normally bulkier and more difficult to dewater. Surface hydraulic loading or surface overflow rate (SOR) is the vertical velocity of the influent in the secondary sedimentation tank ( $m^3/m^2$  of tank surface per hour, m/h). SOR of approximately 0.5  $m^3/m^2$  per hour is generally used for secondary sedimentation of tannery effluents, i.e., less than for primary clarifiers.

Surface solid rate (SSR) is the quantity per hour of MLSS (kg) crossing the surface area of the secondary sedimentation tank (kg/m<sup>2</sup> of tank surface per hour) (see primary sedimentation). SSR values between 2.0 and 3.0 kg/m<sup>2</sup> per hour are generally used for secondary sedimentation of tannery effluents. The overflow from the secondary clarifiers represents the fully treated effluent usually fit for discharge into a final recipient.

In order to satisfy the legal limits for nitrogen (ammonia and TKN), very often nitrification and denitrification stages need to be introduced into the biological system. Nitrification requires extensive aeration as well as a low F: M ratio (< 0.1) to facilitate conversion of nitrogen containing organic matter into nitrate and nitrite salts. During the denitrification stage, which for operational reasons can take place either at the very beginning or at the end of the biological treatment, these salts are converted under anoxic conditions into neutral nitrogen gas (N<sub>2</sub>) and water [A. Itodo1, 2018].

#### 2.10.5 Anaerobic treatment:

Anaerobic treatment of wastewater converts the organic pollutants into a small amount of sludge and large amount of biogas (methane and carbon dioxide). The sulphide present in wastewater inhibits the anaerobic treatment. Methanogenic bacteria are inhibited by sulphide, whereas acidifying and sulphate reducing bacteria do not inhibit. Three inhibiting effects of sulphide or sulphide reduction are known: direct toxicity of sulphide, substrate competition between sulphates reducing and Methanogenic bacteria and precipitation of trace elements by sulphide. The extent of these effects depends on the experimental system used. In a continuous fixed film reactor, the efficiency of degradation was improved by 15% ate hydraulic retention time of 1.9 days when the concentration of undissociated sulphide was reduced from 100 to 30 mg/L.

The Advantage and Disadvantage Anaerobic treatments are Removal of sulphate, sulphite and thiosulphate forme the waste stream, Heavy Metal removal Precipitated metal sulphides and Reduce COD removal efficiency, Corrosion, less methane formation respectively. In two stage anaerobic treatment of tannery wastewater, 30% of the sulphate was reduced independent of the sulphate influent concentration in the first stage. With high concentration of sulphate in influent, percentage of desulfurization decreased in the second stage. Pre treatment of wastewater for reducing the tanning chromium and sulphide levels gives better results in COD removal efficiency. In anaerobic up flow contact filter, COD removal efficiency was in the range of 79-95% after pretreatment compared to 60-86% for untreated wastewater [H. Dargo and A. Ayalew, 2014].

#### 2.11 Advanced (tertiary) treatment

In certain cases, despite extensive physical-chemical and biological treatment in a well designed ETP, the quality of the final effluent does not meet the promulgated discharge limits. The usual culprit is the recalcitrant COD, i.e., compounds that the micro-organisms present in the floc are unable to decompose. In such cases, it is

necessary to resort to additional, usually more sophisticated and rather expensive treatments such as mineralization of organic compounds by oxidation with H2O2 in the presence of ferrous sulphate (Fenton process and its derivatives). Ozonsaion is sometimes included not so much to kill potentially harmful micro organisms but to destroy part of the residual COD [A. Itodo1, 2018].

## **2.11.1 Sludge handling**

## 1/ Mechanical sludge dewatering

The main purpose of sludge dewatering is not only to reduce the volume and weight of material to be transported but also to attain the dry matter content required for disposal at landfills.

The equipment used for this purpose is recessed-plate filters, belt presses and decanter centrifuges – was already described earlier. Here is a short comparative overview of the main characteristics and efficiencies of the various systems as well as changes in DS content throughout the treatment process.

**Table (2-6):** Characteristics of sludge dewatering equipment [N. K. Srivastava and<br/>C. B. Majumder].

Equipment	Decanter	Belt press	Plate –filter press	
Way of operation	continuous	continuous	Batch	
Sludge conditioning	Required <sup>(1)</sup>	Required <sup>(1)</sup>	Not required <sup>(2)</sup>	
Washing water	Not required	Required <sup>(3)</sup>	Not required <sup>(4)</sup>	
Lab our	Only supervision	Only supervision	Required during cake discharge	
Sensitive to sludge variability	sitive to sludge variability Very sensitive		Less sensitive	
Energy demand (electricity )	ergy demand (electricity ) High		Low	
Maintenance	Sophisticated	Medium	Low	

(1) Polyelectrolyte (usually cationic): 2-4 g/kg of DS.

(2) Sludge conditioning with inorganic chemicals (iron salts and lime) is not strictly necessary, but recommendable for enhancing filtration rate and general performance.

(3) About 10 m3/h of clean water at 4 bars per meter of belt width are required for continuous belt washing.

(4) Periodical cleaning of filtering cloth is required (at least once per week) [N. K. Srivastava and C. B. Majumder].

Handling Post-purification, sedimentation and sludge handling are the last step in wastewater from the water phase by gravity settlement. After dewatering this sludge by means of filter presses, a sludge cake with up to 40% dry solids can be achieved, whereas belt presses produce a sludge cake with up to 20-25% dry solids [H. Dargo and A. Ayalew, 2014].

#### 2/ Utilization and disposal

In comparison with sanitary sludges, tannery sludge has greater inorganic matter content, greater heavy metal content, especially chromium and greater sulfur compound content. However, the main stumbling block is the chromium content, with legislation and practice varying a lot from country to country. A number of solutions for utilization and/or safe disposal of tannery sludge have been proposed, practiced, tested, and applied at pilot and industrial scale: landfill, land application, composting, anaerobic digestion, thermal treatment, vitrification, pyrolisys, brick making, etc., none of them proving satisfactory enough. There is certainly no universal solution for sludge utilization/application. Each ETP produces sludge of specific characteristics and different regions and countries have quite different regulations regarding sludge utilization. Therefore, prior to any ETP construction, a detailed assessment of options should be prepared and the most suitable application proposed. In any case, handling, storage and transport of sludge and solid wastes from PTPs and ETPs should also be safe and not contaminate the surroundings; thus, for example, the collection points should be protected against bad weather (rain, for example).

# 2.12 The issue of bad odor

Odours associated with wastewater are difficult to quantify because they are caused by a wide variety of compounds and they are a nuisance that is more qualitative than quantitative. Sensitive persons easily detect very low concentrations of odoriferous substances in the air (sulphides/other sulphur compounds, ammonia, amines, etc.). Local geographic and climatic conditions such as wind direction, land shape, air humidity, ground and air temperature, etc. play an important role. Along the treatment line, the main sources of bad smell are:

- Equalization and sulphide oxidation;
- Sludge thickening;
- Biological aeration;
- In-plant storage of dewatered sludge;
- Temporary sludge disposal site.

Yet, the main source of bad smell remains the stripping of hydrogen sulphide; it is not the concentration of sulphide per se, but the lowering of pH: the not disassociated  $H_2S$  is present only at pH below 10. Thus, it is crucial to control pH and, if needed, alkalis like NaOH or lime are added to achieve pH > 9.5-10. More extensive, uninterrupted aeration may help, but sometimes rigorous (and expensive) methods such as adding hydrogen peroxide or pure oxygen are necessary. Nowadays, in some places, nearly the entire ETP is covered and the air is purified [A. Itodo1, 2018].

## **Chapter three**

## **Materials and Methods**

## **3.1 Introduction**

To achieve the objectives of this study, various methods of data collection, quantitative, and qualitative analyses through observation, reports, books, articles, interviews and internet and samples analyses were used.

## 3.2 Study area

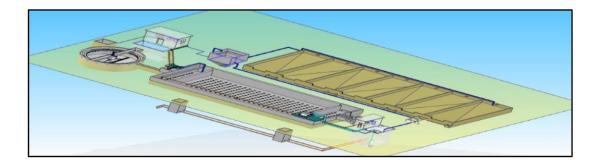
The study area, White Nile tannery is located in the south of the Khartoum, near from the horse race and it was established in 1971, and in 2011 it was purchased by Saria international advanced business company.

The water produced from hides tanning included high amount of hazardous chemical pollutants, so the treatment plant was designed to remove and reduce the hazardous pollutants before entering to the sewage network.

Generally the treatment is divided into three sections:

- 1-Physical treatment (mechanical treatment)
- 2- Biological treatment.
- 3- Chemical treatment.

The main parts of the industrial waste water treatment plant are illustrated below:



## Figure (3-1): industrial waste water treatment plant

## 1- The collection point

It is a basin to collect water produced from tanning under gravity.

### 2- The screen

It is the smooth screen with diameter 1mm and used to remove small and big substances and hides remain from reaching the next stage and keep the pumps from damage. The screen daily cleans by washing pump to avoid clogging.

## 3- Lift station

The group of pumps used to raise the waste water to the aeration tank

## 4- Aeration tanks

It is rectangular basin with the capacity of  $900m^3/day$  and used to remove the organic substances by using microorganisms (reduce BOD and COD). In this basin, oxygen and manganese sulphate are added to the waste water and left from 16 to 32 hours to complete the process of biodegradation.

## 5- Fast mixers basins

They are two basins used to mix waste water with the aluminum sulphate and Pac (poly aluminum chloride)

#### 6- Sedimentation basin

Used to remove the particles produced from added the chemical substances in the previous stage by the earth gravity.

#### 7- Pump station

The purpose is to expose treated water to the sewage network

#### 8- Activated sludge tank

Used to collect sludge and particles produced from sedimentation process

### 9- Dewatering basins

They are seven basins work as sand filter, used to separate water coming with the sediments and then these sediments been dried by sun and wind.

## **3.3 Materials**

The following is a list of the chemicals and reagents used for testing in the research:

NO	Chemical or reagent
1	Sulphuric acid reagent
2	Standard Potassium Dichromate
3	Standard ferrous ammonium sulphate (0.1M)
4	Ferroin Indicator solution
5	Hexane
6	Hydrochloric acid (HCL)

Table (3.1): Chemicals or reagents used

## 3.4. Methods

#### 3.4. 1 Primary data collection methods

The engineers and operators of the White Nile tannery and the industrial waste water treatment plant were interviewed to collect information on the stages of tanning and the stages of industrial wastewater treatment.

#### **3.4.2 Sample preparation**

The samples were taken using sterile glass bottles from specified points in the station as illustrated in the table below:

Samples No:	Source of Sample
1	From the inlet effluent of the station
2	From outlet effluent of the station

 Table (3.2): Samples sources

\*the number of samples determined depended on available cost to analysis those samples.

## **3.5** Characterization of tannery effluent

The sampled effluent was analyzed for their chemical oxygen demand (COD), Biological oxygen demand (BOD), total suspended solids (TSS), total dissolved solid (TDS) power of hydrogen (pH), oil and greases and chrome (Cr).

#### 3.5.1 pH value measurement method

#### **Principle:**

The pH value is found by measurement of the electromotive force. Generated in a cell. It is made up of an indicator electrode which is reactive to hydrogen ions such as a glass electrode. When it is immersed in the test solution the contact between reference electrode (usually mercury/calomel electrode), and the test solution the electromotive force is measured. A pH meter, that is, a high impedance voltmeter is marked in terms of pH. Varieties of electrodes have been suggested for the determination of pH. The hydrogen gas electrode is the primary standard. Glass electrode in Coordination with calomel electrode is generally used with reference potential provided by saturated calomel electrode. The glass electrode system is based on the theory that a change, of 1 pH unit produces an electrical change of 59.1 mV at 25°C. The membrane of the glass forms a partition between two liquids of differing hydrogen ion concentration thus a potential is produced between the two sides of the membrane which is proportional to the difference in pH between the liquids.

#### **Procedure:**

The instrument was standardized after required warm-tip period. A buffer solution of pH near to that of the sample was used. The electrode was checked against at least one additional buffer of different pH value. The temperature of the water was found and if temperature compensation is available in the instruments it is adjusted. The electrodes were rinsed and gently wiped with solution. If necessary, the electrodes are immersed into the sample beaker or sample stream and stirred at a constant rate to provide homogeneity and suspension of solids. Rate of stirring is minimized and the air transfer rate at the air-water interface of the sample was noted. The sample pH and temperature was noted.

#### 3.5. 2 Method of BOD measurement

#### **Principle:**

The B.O.D test is carried out by completely filling two bottles or three with the water or dilution water to be tested. The dissolved oxygen in one of the bottles is then measured by using dissolved oxygen meter or by titration the anther bottles were kept in darkness to prevent photosynthesis was kept at 20 C for five days.

Oxidation and Reduction Reaction:-

Oxidation by bacteria.

 $C_6 H_{12}O_6 + O_2$  Bacteria  $\rightarrow$   $CO_2 + H_2O + Inorganic chemical$ 

#### **Reduction Reaction:**

Manganous sulfate and alkaline potassium iodide are added to the water sample and the two interact producing a white flocculent precipitated of manganous hydroxide.

$$MnSO_4+2KOH \longrightarrow Mn (OH)_2 + K_2SO_4$$
$$Mn^{2+} + 2HO \longrightarrow Mn (OH)_2$$

If a white precipitated obtained, there was no dissolved oxygen in the sample .otherwise in the presence of oxygen the white Mn (OH)2 precipitated would react with  $O_2$  forming a brown precipitate of manganic basic oxide.

 $2Mn(OH)_2 + O_2 \longrightarrow 2MnO(OH)_2.$ 

Upon the addition of conc. sulfuric acid the brown precipitate dissolve forming manganic sulfate.

 $MnO(OH)_2 + 2H_2SO \longrightarrow Mn(SO_4)_2 + 3H_2O$ 

There are numbers of ways to precipitate these brown ppt and may have many formula e.g.  $(Mn (OH)_3, Mn_2O_3, MnO (OH)_2 \dots etc)$ .

There is an immediate reaction of this compound with the previously added KI liberating iodine and produce typical brownish iodine coloration.

$$Mn (SO4)_2 + K_I \longrightarrow MnSO4 + k_2SO_4 + I_2$$

The amount of iodine liberated by the reactions is equivalent to the number of moles oxygen present in the sample .the amount of iodine determined by titration of aliquot portion of the solution with standard sodium thiosulfate solution.

$$Na_2S_2o_3+ I_2 \longrightarrow Na_2S40_6+2NaI$$

Since 1ml of 0.025N sodium thiosulfate is equivalent to 0.2 mg oxygen, the number of ml of sodium thiosulfate used is numerically equivalent to the Concentration in mg/l of DO, if 200 ml of sample is titrated .similarly if 100ml aliquot is used with 0.005N ST titrated ,the ml of titrated \*0.4 would give the mg of  $0_2$  per liter.

Small amount of concentrated  $H_2SO_4$ , free iodine ion from azide to react with manganese (III) hydroxide to liberate iodine as following:

$$2Mn (OH)_3 + 2I^- + 6H_2O \longrightarrow I_2 + H_2O + 2Mn^{2+}$$

#### **Dilution technique :**

Made in several dilutions of the prepared sample to obtain the required depletions. The following dilutions were suggested 0.1 to 1.0% for strong trade waste, 1 - 5% for raw and settled sewage, 5 - 25% for oxidized effluents and 25 - 100% for polluted river or lake waters. The desired volume of distilled water saturated with the D.O was placed in a suitable vessel and 2ml of each of Phosphate buffer, Magnesium sulfate, Calcium chloride and ferric chloride solution were added in liter of water. After addition of the desired quantity of sample to the dilution water

carefully, it was mixed well, avoiding entrainment of air and siphon the mixed dilution was put into two BOD bottles, one for incubation and the other for determination of the initial D.O in the mixture. the first one was closed tightly using Stopper and was incubated for 5days at 20°C.

#### **Determination of the initial D.O:**

The D.O of the initial and that of the final diluted samples & blank (after 5days incubation at 20°C) were determined using the azide modification of the iodometric method.

#### Calculation and result expression as follows:

#### Decimal fraction of the dilution water used

#### 3.5. 3 Method of COD measurement

#### **Principle:**

Most types of organic matter are oxidized by a boiling mixture of chromic and sulfuric acid. A sample is refluxed in strongly acid solution with a known excess of potassium dichromate  $K_2Cr_2O_7$ . After digestion the remaining unreduced amount of  $K_2Cr_2O_7$  consumed and the oxidizable matter is calculated in terms of oxygen equivalent. The reaction involved with dichromate may be represented as:

$$C_{n}H_{a}O_{n} + cCr_{2}O_{7}^{--} + 8cH^{+}\Delta - \frac{1}{2} nCO_{2} + \frac{1}{2} (\underline{a+8c} H_{2}O) + 2cCr^{+3}$$
Where  $c = -\frac{2n}{3} + \frac{a}{6} - \frac{b}{3}$ 

Ferrous ion from ferrous ammonium sulfate is an excellent reducing agent for dichromate in solution, however Fe<sup>++</sup> is slowly oxidized by oxygen and so

standardization must be performed every time prior to titration. The standardization is made with 0.25N solution of dichromate:

 $6 Fe^{++} + Cr_2O_7^{--} + 14 H^+ \longrightarrow 6Fe^{++} + 2Cr^{+3} + 7H_2O$ 

#### **Procedure:**

- 1.5 ml of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was added in the same tube, and then 3.5 ml of H<sub>2</sub>SO<sub>4</sub> reagent were added The total volume of solution in the tube will be 7.5ml, then the tubes were covered and closed firmly and arranged in a steel rake and was put in the oven to digest for 2 hrs at 150°C.
- After the mentioned period, the tube was removed from the oven and let to cool in room temperature, then titrated against FAS 0.1M using 1-2 drops of Ferroin indicator.

#### **Calculations:**

#### COD (mg\l) = blank value – sample value x 8 x 0.1 x 1000

#### Volume of sample

#### 3.5. 4 Method of Total Suspended Solid measurement (TSS)

#### **Principle:**

A well-mixed sample is filtered through a weighed standard glass fiber filter and the residue retained on the filter is dried to a constant weight at 103 to 105°C. The increase in weight of the filter represents the total suspended solids. To obtain an estimate of total suspended solids, calculate the difference between total dissolved solids and total solids.

#### **Procedure:**

#### Preparation of glass fiber filter disk:

disk with wrinkled side was inserted up into filtration apparatus, the disk washed with three successive 20ml of distilled water. The suction was continued to remove traces of water, the vacuum was turned off, and the washings was discarded. It was remove from the filtration apparatus and transferred to an inert aluminum weighing dish. Dried in oven at 103 to 105°C for 1h. Cool in desiccators to balance temperature and weigh. Then stored in a desiccators until needed.

#### Sample analysis:

Sample was put in filtering apparatus and filtered and suctioning began. Wet filter with a small volume of distilled water was used to Wash filter with three successive 10ml, allowing complete drainage between washings, and continue suction for 3minutes after filtration completed. Samples with high dissolved solids may require additional washings. Carefully filter was removed from filtration apparatus and transferred to an aluminum weighed dish as a supported. Dried for at least 1h at 103 to 105°C in an oven, then cooled in desiccators to balance temperature and weigh.

#### **Calculation:**

## Total suspended solids $mg/l = (A-B) \ge 1000$ Sample volume ml

Where:

A= weight of dried residue + filter

B= weight of filter

## **3.5. 5 method of measurement of electro conductivity and Total dissolved Solids (EC and TDS):**

#### **Procedure:**

the electrode was washed thoroughly with water and distilled water, 100 ml of the sample was took and placed in a cup, the electrode was entered in the cup and the readings were recorded.

#### **Calculation:**

Where:

TDS: total dissolved solid (mg/l) EC: electro conductivity (µs/cm)

A: factor –factor range (0.6 -0.7)

#### 3.5.6 Method of measurement of oil and greases

#### **Procedure:**

100 ml of the sample ,30 ml of hexane and 7.5 ml of hydrochloric acid were took and placed in the separation unit; the contents of the unit were mixed well for 2 minutes, the Petri dish was weighed empty  $(w_1)$ , Then the oil was poured in the dish and the water was in the cup, the procedure was performed more than once until all oils and greases are separated from the sample, the dish was took and placed in the oven for 15 minutes at 70 ° C Then the Petri dish was took to humidity absorber for 30 minutes and then weighed $(w_2)$ .

### **Calculation:**

## Oil and grease mg/l = $(w2 - w1)\chi 10^{6}/v$

Where:

 $w_1$ : Weight of the Petri dish  $w_2$ : Weight of the Petri dish and oil V: volume of sample[S,.K.Soni,2013, Clesceri,L.S.et al, 1998].

#### **3.5.7 Method of measurement of chrome (Cr)**

The amount of chrome was determined by using inductively coupled plasma device (ICP).

## **3.6 Equipments**

The devices which were used for determination of wastewater characteristics are:

**1-PH meter** -with glass and reference electrode (saturated calomel), preferably with temperature compensation. Thermometer - with least Count of  $0.5^{\circ}$ C.

#### **2-TSS determination Apparatus**

- Glass fiber disks.
- Filtration apparatus.
- Analytical balance.
- Desiccators.
- Measuring cylinder, pipette, and beaker.
- Aluminum weighing dish.
- Drying oven for operation at 103- 105°C.

-

# **3-** Electro conductivity and Total dissolved Solids (EC and TDS) determination Apparatus:

-Cup - Conductivity meter.

## 4- Oil and greases determination Apparatus:

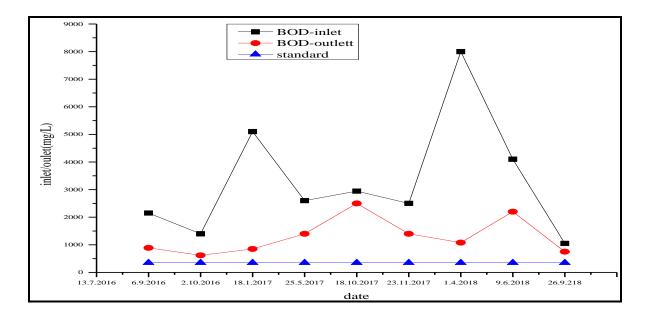
- Flask, Petri, Oven
- Humidity Absorber
- Sensitive Balance
- Separation Funnel

## **Chapter four**

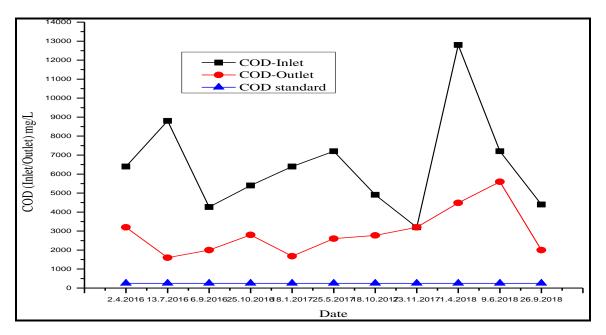
## **Results and discussions**

# **4.1 BOD and COD concentrations in the inlet and outlet effluents of the treatment station**

Biochemical oxygen demand (**BOD**) and chemical oxygen demand (**COD**) used as indicators for the amount of organic substances found in the wastewater and to measure the efficiency of the biological treatment for the sewage plant. It can be observed From the samples results taken from 2016 to 2018 in **figure 4.1** and **4.2** that the minimum concentration of **BOD** and **COD** after treatment are (**620**, **1600 mg/l**) respectively, Taking into consideration that the allowable limit for concentration of **BOD** and **COD** in Sudanese standards for disposal of industrial wastewater in sewage network are (**350,250 mg/l**) respectively as in a **table (4-1)**. So the high values of **BOD** and **COD** after treatment compared with the standard limits indicate that the biological treatment is not efficient as required and the **BOD** and **COD** removal efficiency should be increased by mixing sewage with industrial wastewater to increase the amount of microorganisms, and the duration of treatment should be increased also from 16 hr to 32 hr to reduce concentrations of organic pollutants.



**Figure (4-1)** BOD concentrations in the inlet and outlet effluents of the treatment station from 2016 to 2018 compared with the standard of disposal in sewer system.



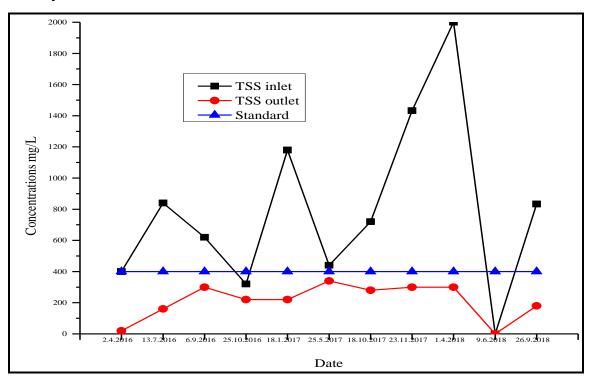
**Figure (4-2)** COD concentrations in the inlet and outlet effluents of the treatment station from 2016 to 2018 compared with the standard of disposal in sewer system

## 4. 2 TSS concentrations in the inlet and outlet effluents of the

#### treatment station

Total suspended solid (**TSS**) is used as indicator for the amount of impurities found in the wastewater, and to measure the efficiency of the sedimentation process for the sewage plant. From **figure 4.3** it was noticed that the maximum concentration of **TSS** after treatment is

(**340 mg/l**), and by comparing this value with the allowable limit of **TSS** in Sudanese standards for disposal of industrial wastewater in sewage network of **400 mg/l** as in a **table (4-1)**. It was found that the **TSS** values meet the requirement of the Sudanese standard and these means that the sedimentation process works efficiently.

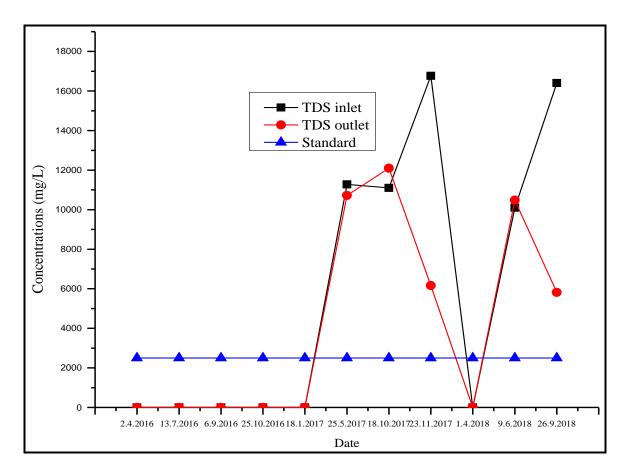


**Figure (4-3)**: TSS concentrations in the inlet and outlet effluents of the treatment station from 2016 to 2018 compared with the standard of disposal in sewer system.

## 4. 3 TDS concentrations in the inlet and outlet effluents of the

## treatment station

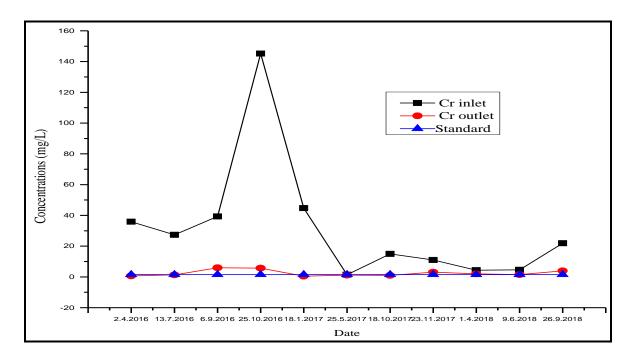
Total dissolved solid (**TDS**) used as indicator for the chemical substances dissolved in the wastewater. And it is very important indicator for the wastewater produced from the tanneries. From **figure** (**4**-**4**) it was realized that the minimum concentration of **TDS** after treatment is (**5820 mg/l**), and by comparing this value with the limit of Sudanese standard for disposal of industrial wastewater in sewage network which is about (**2500 mg/l**) as in a **table** (**4**-**1**) it was obvious That the **TDS** is very high therefore a reverse osmosis unit or any system are required to be added to the station to reduce the concentration of **TDS**.



**Figure (4-4):** TDS concentrations in the inlet and outlet effluents of the treatment station from 2016 to 2018 compared with the standard of disposal in sewer system.

## 4. 4 Cr concentrations in the inlet and outlet effluents of the treatment station:

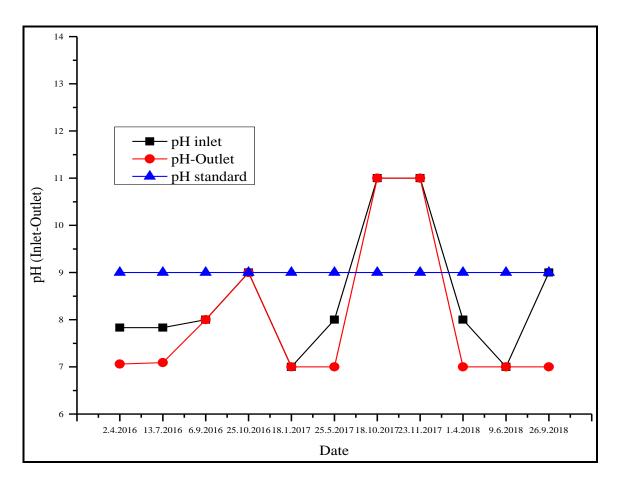
The main process in the tanning is the process of using chromium, which is consider one of the heavy metals and well known carcinogenic substance, therefore the concentration of it in must be measured before disposal of the effluent in sewer system. From the samples results taken from 2016 to 2018 in **figure (4-5)** it was found that the minimum and maximum concentration of **Cr** after treatment are (**0.65**, **5.94 mg/l**) respectively, whereas the allowable limit of **Cr** concentration in Sudanese standards for disposal of industrial wastewater in sewage network is (**1.5 mg/l**) as in **table (4-1)**. Through the results obtained for the years mentioned it is found that there is a variation in **Cr** values, some values meet the requirement of the Sudanese standard and others are higher than the allowable limit, therefore, there is a need for a unit in the treatment plant to recover the chromium (**Cr**) and reuse of it in the tanning process again.



**Figure (4-5):** Cr concentrations in the inlet and outlet effluents of the treatment station from 2016 to 2018 compared with the standard of disposal in sewer system.

## **4. 5** pH values in the inlet and outlet effluents of the treatment station

The **pH** values are used to measure the acidity or alkalinity of a fluid. From **figure** (**4-6**) it was observed that the minimum and maximum values of **pH** of the samples in the years from 2016 to 2018 are (**7**, **11**) respectively which are higher than that of the Sudanese standard which vary **from 6 to 9** as in a **table (4-1)** .these high values can cause problems in the biological treatment unit in the system of sewer treatment stations, therefore a **pH** controller unit should be added to the treatment station.



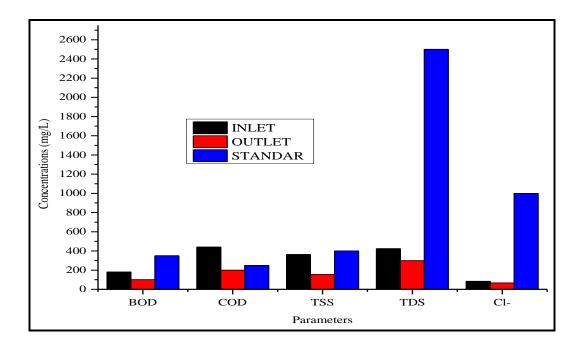
**Figure (4-6):** pH values in the inlet and outlet effluents of the treatment station from 2016 to 2018 compared with the standard of disposal in sewer system.

## **4.6 Investigation of the results of tests conducted on the effluent entering (inlet) and leaving (outlet) the treatment station:**

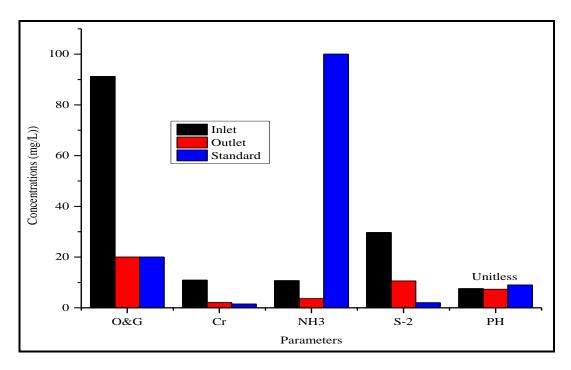
**Figure (4-7)** and **Figure (4-8)**, show that the concentrations of pollutants in the effluent leaving the treatment plant to the sewage network are meet the requirement of Sudanese standard of disposal of industrial wastewater in sewage network except the concentration of chromium, which is higher than the standard. Taking into account that the sampling was taken during a period that the processes of pre tanning were completely stopped and the effluent leaving the tannery is as a result of only tanning operations and finishing processes therefore, these explain the results of the samples that were obtained in relation to their compliance with the Sudanese standards and the high chromium concentration.

 Table (4-1): Samples results

parameter	BOD <sub>5</sub>	COD	TSS	TDS	PH	0& G	Cl-	Cr	NH <sub>3</sub>	S-2
Inlet	180	440	363	423	7.58	91.2	84	10.9	10.7	29.7
Out let	100	200	155	299	7.3	20	67	2.04	3.6	10.6
Standard	350	250	400	2500	9	20	1000	1.5	100	2
Plant efficiency%	60.83	55	73.6	31	accept	78.1	accept	92.3	accept	64.3
<b>Requirement efficiency%</b>	89.45	96.13	54.5	81	accept	78.1	accept	95.3	accept	93.3



**Figure (4-7):** Concentration of BOD, COD, TSS, TDS and Cl- in wastewater entering (inlet) and leaving (outlet) the treatment plant compared with the standard



**Figure (4-8):** Concentration of Cr, NH<sub>3</sub>, O&G, S<sup>-2</sup>, Cl<sup>-</sup> and pH values in wastewater entering (inlet) and leaving (outlet) the treatment plant compared with the standard

## **Chapter five**

## **Conclusion and recommendations**

## **5.1. Conclusion:**

Tannery wastewater is difficult to treat because of complex characteristics like high BOD, COD, suspended solids, sulphide and chromium. The main purpose of this study is to assess the performance of the industrial wastewater treatment plant for the White Nile tannery and to ensure that the water disposing from this plant meet the requirements of Sudanese standards. Based on the results obtained from the study, the following conclusions can be drawn:

- High values of BOD and COD after treatment compared with the standard limits indicate that the biological treatment is not efficient as required.
- The BOD and COD removal efficiency should be increased by mixing sewage with industrial wastewater to increase the amount of microorganisms, and the duration of treatment should be increased also from 16 hr to 32 hr to reduce concentrations of organic pollutants.
- The TSS values meet the requirement of the Sudanese standard and these means that the sedimentation process works efficiently.
- The TDS is very high therefore a reverse osmosis unit or any system is required to be added to the station to reduce the concentration of TDS.
- There is a variation in Cr values, some values meet the requirement of the Sudanese standard and others are higher than the allowable limit, therefore, there is a need for a unit in the treatment plant to recover the chromium (Cr) and reuse of it in the tanning process again.

• The minimum and maximum values of pH of the samples are higher than that of the Sudanese standard .these high values can cause problems in the biological treatment unit in the system of sewer treatment stations, therefore a pH controller unit should be added to the treatment station.

### 5.2. Recommendations:

- 1- Laboratory tests should be performed periodically to ensure that the properties of treated industrial wastewater meet the requirements of Sudanese standard for wastewater disposal in sewage network.
- 2- A pH unit should be added to the treatment plant to ensure the efficiency of biological treatment.
- 3- Biological treatment time should be increased to reduce organic pollutants.
- 4- Modern techniques should be introduced that enable recovery and reuse of chromium which considered one of carcinogen heavy metals.

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## Appendix

## A

**Table 4-2:** Maximum limits for concentration of industrial waste water pollutants

number	Parameters	Unit	Standard A	Standard B
1	PH	-	6-9	6-9
2	BOD <sub>5</sub>	mg/l	350	100
3	COD	mg/l	250	250
4	TSS	mg/l	400	200
5	CL-	mg/l	1000	600
6	N-NO <sub>3</sub> -	mg/l	60	40
7	TDS	mg/l	2500	1500
8	$SO_4^{-2}$	mg/l	300	350
9	S <sup>-2</sup>	mg/l	2	2
10	O&G	mg/l	20	10
11	Р	mg/l	20	20
12	Cr	mg/l	1.5	0.1
13	Cn	mg/l	0.5	0.2
14	Fe	mg/l	2	1
15	Zn	mg/l	5	5
16	Cu	mg/l	2.5	0.5
17	Mn	mg/l	0.1	0.05
18	NH <sub>3</sub>	mg/l	100	100
19	As	mg/l	0.5	0.25
20	Ba	mg/l	3	1.5

[SSMO, 2008]

21	Во	mg/l	1	0.5
22	Со	mg/l	0.5	0.5
23	Pb	mg/l	0.1	0.015
24	Mg	mg/l	100	50
25	AL	mg/l	10	5
26	Hg	mg/l	0.02	0.005
27	Ni	mg/l	1	0.5
28	Se	mg/l	0.5	0.3
29	Ag	mg/l	1	0.5
30	Na	mg/l	500	200
31	Total coliform	Count/100ml	1	0
32	Aerobic plate count	Count/100ml	1000	500

Standard A: The maximum limits of pollutants with industrial wastewater that can be discharged to the sewage network.

Standard B: The maximum limits of pollutants with industrial wastewater that can be discharged to the environment.

**Table4-3:** PH values in the inlet and outlet effluents of the treatment station from 2016to 2018 compared with the standard of disposal in sewer system.

Date	2.4.2016	13.7.2016	6.9.2016	25.10.2016	18.1.2017	25.5.2017	18.10.2017	23.11.2017	1.4.2018	9.6.2018	26.9.2018
Inlet	7.83	7.83	8	9	7	8	11	11	8	7	9
Outlet	7.06	7.09	8	9	7	7	11	11	7	7	7

**Table 4-4:** COD concentrations in the inlet and outlet effluents of the treatment station from 2016 to 2018 compared with the standard of disposal in sewer system.

Date	2.4.2016	13.7.2016	6.9.2016	25.10.2016	18.1.2017	25.5.2017	18.10.2017	23.11.2017	1.4.2018	9.6.2018	26.9.2018
Inlet	6400	8800	4266	5400	6400	7200	4906.5	3200	12800	7200	4400
Outlet	3200	1600	2000	2800	1680	2600	2773	3200	4480	5600	2000

**Table 4-5:** BOD concentrations in the inlet and outlet effluents of the treatment stationfrom 2016 to 2018 compared with the standard of disposal in sewer system.

Date	2.4.2016	13.7.2016	6.9.2016	25.10.2016	18.1.2017	25.5.2017	18.10.2017	23.11.2017	1.4.2018	9.6.2018	26.9.2018
Inlet	-	-	2150	1400	5100	2600	2943.9	2500	8000	4100	1050
Outlet	-	-	890	620	850	1400	2500	1400	1080	2200	750

**Table 4-6:** Cr concentrations in the inlet and outlet effluents of the treatment stationfrom 2016 to 2018 compared with the standard of disposal in sewer system.

Date	2.4.2016	13.7.2016	6.9.2016	25.10.2016	18.1.2017	25.5.2017	18.10.2017	23.11.2017	1.4.2018	9.6.2018	26.9.2018
Inlet	35.85	27.33	39.34	145.2	44.725	1.411	14.98	10.979	4.360	4.627	21.86
Outlet	0.65	1.29	5.940	5.738	0.437	1.113	0.98	3.050	1.975	1.479	3.95

**Table 4-7** TSS concentrations in the inlet and outlet effluents of the treatment stationfrom 2016 to 2018 compared with the standard of disposal in sewer system.

Date	2.4.2016	13.7.2016	6.9.2016	25.10.2016	18.1.2017	25.5.2017	18.10.2017	23.11.2017	1.4.2018	9.6.2018	26.9.2018
Inlet	400	840	620	320	1180	440	720	1433	2000	-	833
Outlet	20	160	300	220	220	340	280	300	300	-	180

**Table 4-8:** TDS concentrations in the inlet and outlet effluents of the treatment stationfrom 2016 to 2018 compared with the standard of disposal in sewer system

Date	2.4.2016	13.7.2016	6.9.2016	25.10.2016	18.1.2017	25.5.2017	18.10.2017	23.11.2017	1.4.2018	9.6.2018	26.9.2018
Inlet	-	-	-	-	-	11280	11100	16766	-	10100	16400
Outlet	-	-	-	-	-	10720	12100	6160	-	10480	5820

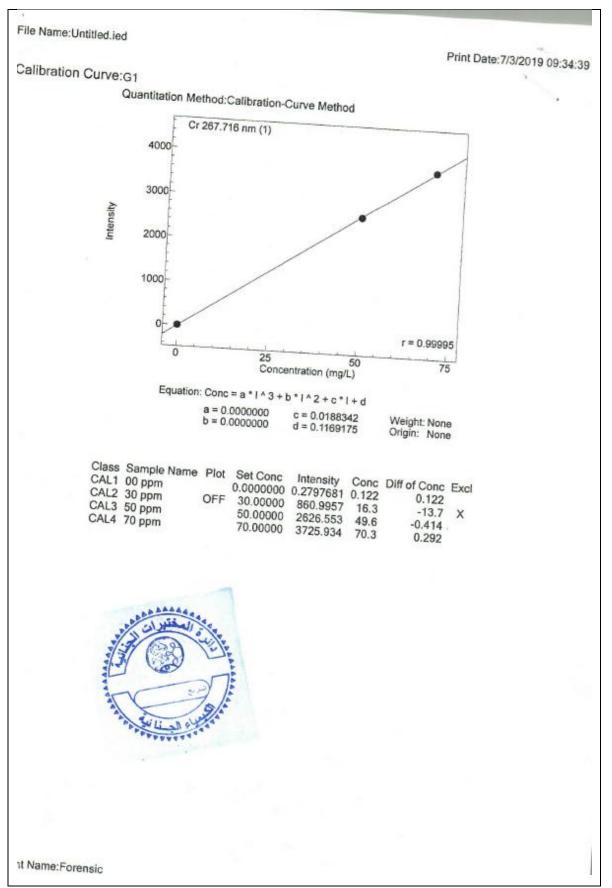


## Sample result analysis of industrial waste water treatment plant for White Nile tannery before treatment

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Samples results analysis of industrial waste water treatment plant for White Nile tannery by using ICP device

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Cr(Dissolved)	A\ azim ELdawi	Eng. Anwar	Mohamed zebair
Cr(Dissolved)	A\ azim ELdawi « Chemistry Lab <sub>3</sub> D	A	Mohamed zebair al Manager
Cr(Dissolved)		A	
Cr(Dissolved)		A	



وزارة البنسى التحتية والواسسلات شركة المختبر ات الإنشائية والبيشية المحدودة CONSTRUCTIONAL & ENVIRONMENTAL LABS.Co.Ltd

ولاية الخرطون

# Test Report

Ref Date	: 18/10/2017
Customer	مدير عام شركة اللين الابيض للصباعات الجلدية :
Sample Type	: Industrial Waste Water.
Source	In let & Out let.
Test required	: as below
<b>Received Date</b>	: 26.9.2017
Reference	: Standard Methods for the Examination of Water and Waste Water.
Remarks	: Sample Collected and Brought by Our Staff.

Test	Unit	Result		
		In let	Out let	
РН	pH-unit	11	11	
EC	μs/cm	15680	17440	
BOD	Mg/L	2943.9	2500	
COD	Mg/L	4906.5	2773	
TSS	Mg/L	720	280	
TDS	Mg/L	11100	12100	
Cr	Ppm	14.98	0.98	

Thank you

# Supervised By

A\ Adeela A\ azim ELdawi

Environmental & Chemistry Labs Director

Eng. Anwar Mohamed zebair General Manager

رقم المطالبة : 2867

Copy to:-

Environmental & Chemistry Labs Director.



and the

ولاية الخرطوم وزارة البنـــــى التـحتيـة والمواصــ

### شركة المختبرات الإنشائية والبيئية المحدودة CONSTRUCTIONAL & ENVIRONMENTAL LABS.Co.Ltd

# Test Report

- Ref Date Customer Sample Type Source Test required Received Date Reference Remarks
- : 23/11/2017 : شركة النيل الابيض للصناعات الجلدية : Industrial Waste Water. :In let & Out let. : as below

: 6.12.2017

- : Standard Methods for the Examination of Water and Waste Water.
- : Sample Collected and Brought by Our Staff.

Test	Unit	Result		
		In let	Out let	
РН	pH-unit	11	11	
EC	μ s/cm	19990	2020	
BOD	Mg/L	2500	1400	
COD	Mg/L	3200	3200	
TSS	Mg/L	1433	300	
TDS	Mg/L	16766	6160	
Cr	Ppm	10.979	3.050	

Thank you

Supervised By A\ Adeela A\ azim ELdawi Environmental & Chemistry Labs Director

Eng. Anwar Møhamed zebair General Manager

Copy to:-

Environmental & Chemistry Labs Director.

رقم المطالبة : 2900

#### Date: 16.4.2018

OUR/REF CELC / 57/13/16

## **Test Report**

**Ref Letter** : 1/4/2018 مدبغة التيل الابيض للصناعات الجلدية : Customer Source :In let - Out let : 22/3/2018 **Received date** Sample Type : Industrial Waste Test required : as below **Test Reference** : Standard Methods for the Examination of Water and Waste Water. Remarks : Sample Collected and Brought by our Staff.

Test	Unit	In let	Out let
РН	pH-unit	8.0	7.0
EC	ms/cm	16.96	16.61
BOD	mg/L	8000	1080
COD	mg/L	12800	4480
TSs	mg/L	2000	300
Cr	Ppm	4.360	1.975

Thank you

Supervised By

A\ Adeela A\ azim ELdawi Environmental & Chemistry Labs Director Copy to:-

- Environmental & Chemistry Labs Director.

Eng. Anwar Mohamed zebair General Manager

رقم المطالبة: 3019

### Date: 23.7 2018

### OUR/REF CELC / 57/13/16

# Test Report

Ref Latter	: 9/6/2018
Customer	شركة الذيل الابيض للصناعات الجلدية :
Sample Type	: Industrial Waster Water
Source	Inlet & Outlet
Test required	: as below
<b>Received Date</b>	: 3.7.2018
Reference	: Standard Methods for the Examination of Water and Waste Water.
Remarks	: Sample Collected and Brought by Our Staff.

Test	Unit	Result		
		In let	Out let	
PH	pH-unit	7	7	
BOD	Mg/L	4100	2200	
COD	Mg/L	7200	5600	
TDS	Mg/L	10100	10480	
Cr	Ppm	4.627	1.479	

Thank you

Supervised By A\ Adeela A\ azim ELdawi Eng. Anwar Me Environmental & Chemistry Labs Director General I

Eng. Anwar Mohamed zebair General Manager

Copy to:-

- Environmental & Chemistry Labs Director.

رقم المطالبة : 3030

#### Date: 28.10 2018

#### OUR/REF CELC / 57/13/16

### Test Report

Ref Letter	: 26 . 9.2018
Customer	شركة النيل الابيض للصناعات الجلديه:
Sample Type	: Industerial waste water.
Source	: Inlet & outlet
<b>Received Date</b>	: 26.9.2018
<b>Test Required</b>	: as below.
Reference :	Standard Methods .
Remarks :	Sample Collected by our staff.

Test	Unit	Result	
Test		Inlet	Outlet
pH	pH-unit	9	7
Ec	μ s/cm	13390	23400
BOD	mg/L	1050	750
000	mg/L	1st 7200	5600
COD		2nd 4400	2000
TDS	mg/L	16400	5820
TSS	mg/L	833	180
Cr	mg/L	21.86	3.95

Thank you

Supervised By A\Adeela A\ azim ELdawi Environmental & Chemistry Labs Director General Manager

Copy to:- Environmental & Chemistry Labs Director.

رقم المطالبة : 3049

• Waste water characteristics of industrial waste water treatment plant for White Nile tannery (2016 -2018):