POLLUTANT LEVELS IN WASTE WATER FROM TANNERY EFFLUENT: A CASE STUDY OF NAKURU TANNERS, KENYA

By

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DECLARATION

Declaration by the Candidate

I hereby declare that this thesis is my original work and has not been presented for a degree in any other University. No part of this thesis may be reproduced without the permission of the author or the University of Eldoret.

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DEDICATION

I dedicate this thesis to the Almighty God who graciously gave me the strength, knowledge, and patience to complete this study.

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ABSTRACT

Wastewater from leather processing industries is very complex and leads to water pollution if discharged before treatment, especially due to its high organic loading and chromium content. Over the past years, Nakuru Tanners Ltd has been discharging raw effluents into the Ndarugo River causing pollution of surface waters, groundwater and soil. Since the water from this river is used for drinking, agricultural and industrial purposes, the assessment of the effluents is necessary. A study to determine the level of toxicants in Nakuru tannery wastewater discharged to the environment has been undertaken. Water samples from four sampling points (S1 – pre-tanning, S2 – tanning, S3 – post-tanning and S4 – drainage to the river) were collected and analyzed. A comprehensive experimental evaluation of tannery wastewater was performed as a basis for the determination of the levels of different pollutants, BOD, COD, pH, turbidity, TSS, NO_3^- and NO_2^- and the values obtained were compared to the standards set by NEMA and WHO. The levels of the metals chromium, iron and lead were determined using FAAS, Kjeldahl method was used for the quantization of NO_3^-, NO_2^- and P determined by Mehlich II extraction while UV-Vis was used in colour determination. The results show that sampling point S1 (wastewater from the pre-tanning stage) recorded the highest parameter levels for pH, TSS and SO_4^{2-} of 11, 294.40 mg/L and 318.50 mg/L, respectively. Sampling point S2 had the highest levels of COD, BOD, Cr and Pb with corresponding values of 9,107 mg/L, 9,150 mg/L, 945 µg/L and 6.50 mg/L. Sampling point S3 recorded the highest parameters of temperature, DO, Fe, P and electrical conductivity of values 24.62 ^{0}C, 1.15 mg/L, 5.40 mg/L, 12.40 mg/L and 14720 μSCm^{-3} while S4 recorded the highest of NO_3^- and NO_2^- pollutants with respective values of 85.20 mg/L and 146.70 mg/L. These levels were, however, above the recommended values set by WHO and NEMA for such parameters in tannery waste water. The company should therefore take immediate counteractive actions to lower these levels of the toxicants in order to avert the associated effects to human and environment. This study has made various recommendations which if undertaken will help make the tannery effluents safe before disposal.

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LIST OF ABBREVIATIONS

ASALs	Arid and Semi-arid Lands
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
DPC	Dynamic People Consulting
DF	Degree of Freedom
EAC	East African Communities
ELISA	East and Southern Africa Leather Industries Association
FAO	Food and Agriculture Organization
FNU	Formazine Nephelometric Unit
F	Statistical Test
GDP	Gross Domestic Product
GOK	Government of Kenya
IPAR	Institute of Policy Analysis & Research
ITC	International Trade Commission
LNCDP	Lake Nakuru Conservation and Development Project
MS	Mean Square
NEMA	National Environment Management Authority
NTU	Nephelometric Turbidity Units
P	Probability Value
SS	Sum of Squares
TDS	Total Dissolved Solids

TSS	Total Suspended Solids
UNCTAD	United Nations Conference on Trade and Development
UNEP	United Nation Environmental Program
UNIDO	United Nations Industrial Development Organization
WHO	World Health Organization
WTO	World Trade Organization

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

The tanning industry represents an important sector in the economy of many countries. On the other hand, depending on the leather process, it generates large quantities of wastewater with ammonium, sulphates, surfactants, acids, dyes, sulphonated oils and organic substances, heavy metals Cr, Pb and natural or synthetic tannins (Schrank *et al.*, 2004; 2005; Kurt *et al*., 2007; Preethi *et al.*, 2009).

These chemical substances are applied to transform the animal skin into products with great capacities for dyeing, as well as to increase the mechanical and hydrothermal resistance. Considering that the greater part of these organic compounds are resistant to conventional chemical and biological treatments, the wastes discharged into natural waters increase environmental pollution and associated health risks. The treatment of this type of wastewater is very complex mainly because of the variety of chemical products added in different concentrations (Schrank *et al.*, 2004; 2005; Kurt *et al.*, 2007; Preethi *et al.*, 2009). The fact that environmental legislation is very strict in almost all countries that are leather producers, a great deal of effort has been made to develop treatments for and remediation of the contaminated environments.

Several methods have been described in the literature, such as direct recycling, coagulation, flocculation, chemical precipitation, ion-exchange, adsorption, biological treatment, electrochemical treatment, membrane separation, thermal techniques and others. Physical chemistry processes, such as coagulation/flocculation, adsorption and

membrane separation, have been the most utilized for the removal of coloured effluents. However, these treatments do not solve the problem because of the transfer of contaminants from one phase to another. However, in biological treatment, the microorganisms degrade the organic pollutants using them as a carbon source to produce metabolic energy for their survival (Song *et al.,* 1999; 2004 and Guo *et al.,* 2006). The pollution of aquatic environment is important because of its significant relation with public health. Some of the main pollutant sources are the industries, which take the natural river water and treated in different steps before draining out to the river.

In some cases chemical pollutants, without any treatment, are drained to the river. This study was therefore aimed at establishing some of the aquatic and environmental effects of the waste released and water discharged from Nakuru Tanners to the environment both the surrounding and the dumpsite within the company before disposal to river Ndarugo in Nakuru town. Nakuru town is located in an environmentally sensitive area. It is sandwiched between Lake Nakuru National Park to the south and the Menengai crater and its associated volcanic landscapes. The population of Nakuru has been growing at the rate of 5.6% per annum and it is considered the fastest growing town in Kenya. Its population is estimated to be 500 000 (Nakuru Municipal council 2012).

1.2 Tannery treatment at Nakuru tanners

The process of waste water treatment at the tannery goes through some steps in order to meet the standards set by the World Health Organization (WHO) and National Environmental Management Authority (NEMA). This involves screens that reduce discharge of harmful wastes from one screen to the other, thus enable settlement of the big particles. In the tannery the first step is removal of particles from water by screens.

This is through separating alkaline (base) liquor from acidic liquor to enhance harvesting of chrome (semi-processing) and upon finishing it is neutralized.

1.2.1   Procedure for harvesting chrome

The tank is divided into five sections.

Section one allows chrome to mix with calcium hydroxide $Ca(OH)_2$ (lime). This reacts with chrome particles to make them heavy. The lime attracts chrome making it heavy for settlement.

The first two chambers aid in mixing of the chemicals while the last two chambers receive clean H_2O that enhances the process of mixing the chemicals. The last chamber settles down the chemicals while the H_2O above moves out to the equalization tank.

1.2.2 Equalization tank

- In this tank, liquor from basic chemicals like high pH and the acidic liquor with a pH of 5 are mixed hence the tank neutralizes the chemicals.

- Introduction of hydrogen sulphide (H_2S) and aluminum sulphate ($Al_2(SO_4)_3$), which helps to settle down any extra uncontrolled particles that evaded collection

- The blower assists in mixing the liquor and chemicals

- The constituent of this tank is left for two to three days for settlement

- The floating liquor is suspended/succeeded out to the sedimentation tank

1.2.3 The sedimentation tank

- Here the sludge is allowed to settle for sometime before being discharged to the drying beds

- The chrome left in the tank is removed to the chrome drying beds

- All the wastes are first dried before disposal in the municipal dump site

■ The waste water is drained to the river (Ndarugo)

1.3 Statement of the Problem

The operation of tannery industries in Kenya is causing severe environmental degradation due to the disposal of untreated effluent on land and in water bodies. There is urgent need for the proper treatment of tannery effluent prior to their disposal (Kiruthu, 2002).

About 130 different types of chemicals are applied in leather manufacturing (Ates *et al*., 1997). Wastewater from leather production is known to be heavily loaded with numerous contaminants, which cause diseases for aquatic organisms, hazardous public health, and a serious threat to the environment (Kiruthu, 2002). Therefore this study sought to determine the identity and the amount of toxic chemicals applied in the processing of the skins in Nakuru tanners located in town. Such a leather industry can cause immense effects not only to the environment but also to the inhabitants of the area including memory loss, increased allergic reactions, high blood pressure, depression, mood swings, irritability, poor concentration, aggressive behaviour, sleep disabilities, fatigue, speech disorders, high blood pressure, vascular occlusion, neuropathy, auto-immune diseases, and chronic fatigue are just some of the many conditions resulting from exposure to such toxins (Tunay *et al*., 2006).

1.4 Justification

The lack of proper wastewater treatment and effluent disposal results in the production of carbon dioxide (CO_2) and methane (CH_4) without the opportunity for carbon sequestration and energy recovery, with deleterious effects for global warming. Without extending wastewater treatment to all urban areas worldwide, CO_2 and CH_4 emissions associated with wastewater discharges could reach the equivalent of 3.13×10^5 CO_2 M^3 d^-

[1] in 2025, with even more dramatic impact in the short-term (Rosso and Stenstrom, 2008).

Although government, at various levels in developing countries, and through its various programs and agencies, has made it a priority in providing portable water for its urban and rural populace through the sinking/drilling borehole water, there is need to address the fate of the water generated after it has met its primary purpose of house hold use. Currently, wastewater management has been perceived as the channeling of wastewater to drainage points which are mainly water bodies and virtually little has been carried out to check the pollution load carried by the wastewater generated, and the environmental and health hazards created by wastewater (Rosso and Stenstrom, 2008). This assesses the pollutant levels, their implication on environment and creating awareness therefore making it necessary to avoid eventual hazards which could be irreversible.

1.5 Objectives

1.5.1 General objective

To ascertain the level of different pollutants in the effluents from Nakuru Tanners limited.

1.52 Specific Objectives

1) To determine the levels of toxicants in the tannery effluent.
2) To assess the effectiveness of waste water treatment from the tannery effluent.

CHAPTER TWO

LITERATURE REVIEW

2.1 Historical Developments of Tanning

Leather tanning is the process of converting raw hides and skins into leather (Covington, 1997). Tanning is claimed to be the second oldest profession in the world. In ancient times, tanning was considered as a noxious trade (Possehl, 1996). 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 (Heidemann and Roether-Eduard., 1993). 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 (UNIDO, 2000).

2.2 Tanning Industry: A Global Outlook

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 (ITC, 1999 and FAO, 2001). Its major expansion has taken place in developing and newly industrialized countries rather than in developed economies (ITC, 1999).

In developing and newly industrialized countries solid waste and wastewater treatments are not state of the art and there is a high labour content to the processes involved in the

conversion of hides and skins into leather (Tchobanoglous *et al*., 2003). The United States, Germany, and other European countries remain major importers of leather products while China, India, Thailand, and Indonesia dominate the export of leather and leather products (ITC, 1999 and FAO, 2001).

2.3 Leather Industry in Kenya

Kenya has a profound tradition of processing leather. In this industry, presently, the rise of the tanneries from nine to eleven with two more under urgent revamping is a sign that the industry is poised for growth. This has further been demonstrated in the recent economic survey of 2008 that showed a 10.3% growth in the leather sector (Muchangi, 2012). Kenya has the potential to generate sizeable export earnings from the leather industry owing to its annual production of hides and skins.

The industry depends largely on the locally available large livestock resource base where the Arid and Semi-Arid Lands (ASALs) covering 70% of the country continues to be a major contributor of slaughter stock where hides and skins are the byproducts. The hides, skins, and leather industry contribute an estimated 4% to agricultural GDP (Heidemann and Roether-Eduard, 1993).

The tanning industry in Kenya is faced with a number of challenges regarding negative environmental implications. In 2008, NEMA ordered the closure of two tanneries over poor disposal of effluents that were leading to pollution of the environment (GOK, 2010). Concerns are growing over dangerous and harmful aspects of some chemicals that are used in the leather-tannery industry and the manner in which effluents from the industry including toxic substances such as chromium salts are being disposed of. Tannery effluents have been an environmental and health hazard, they contain large quantities of

organic and inorganic compounds (Heidemann and Roether-Eduard, 1993). Poorly treated effluents from the tannery industry used for irrigation have led to wide spread contamination of food chains, sharp decline in productivity of food crops, soil, vegetables, and livestock including milk production (Muchangi, 2012).

This has initiated a debate on the need for regulating the tannery industry to be able to protect public health and the environment from harmful impacts of the industry. Continued growth of the industry in the country under a liberalized economy has also dictated the need for effective and well-equipped regulating institutions (Heidemann and Roether-Eduard, 1993).

The Kenya constitution (chapter eight pages 55-59) has several provisions affecting the tanning industry referring to trade, human health and the environment. These include:

- To take all measures to prevent or minimize damage and destruction to land, air, and water resources resulting from pollution or any other kind of natural resource degradation.
- To take all practical measures to promote good water management system at all levels;
- To promote sustainable development and public awareness of the need to manage land, air, water resources in a balanced and sustainable manner for the present and future generations.
- Under Article 39 every person has a right to a clean and healthy environment.

- To provide for measures intended to protect and preserve the environment from abuse, pollution and degradation; to manage the environment for sustainable development; and to promote environment awareness.

Though the existence of these policies is well known in the tannery sector, they are not adhered to mainly because the enforcement is missing.

2.4 The Entire Tanning Process

2.4.1 Pre-tanning Process/Beam house Operations

These are the processes performed to prepare the skins/hides for the real tanning process. They include:

2.4.1.1 Soaking

The purposes of soaking are to clean the skins and remove salt and preservative, to allow the skin to re-absorb some of its lost water and to dissolve out some soluble proteins. Inadequate soaking can cause problems in liming but too much soaking can rob the skin of desirable substance (Covington, 1997; Heidemann and Rother-Edward, 1993).

2.4.1.2 Fleshing and trimming

In this case, the extraneous tissue is removed. Dehairing is done by chemical dissolution of the hair and epidermis with an alkaline medium of sulphide and lime (Wiemann *et al*., 1998). After skinning at the slaughterhouse, the hide appears to contain excessive meat, fleshing usually precedes dehairing and liming (Covington, 1997; Heidemann and Rother-Edward, 1993).

2.4.1.3 Bating

The de-haired, fleshed and alkaline hides are neutralized (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 (Heidemann and Rother-Edward, 1993, Covington, 1997 and Mumford, 2010).

2.4.1.4 Pickling

This is an acid bath treatment in which skins are prepared for bleaching and tanning with synthetic tans (syntans) or mineral tans. Classic skins can be pickled in a pit for about two days but ossified skins undergo a special pickling to remove the bone deposits as much as possible. This process takes several days and is best done with the skins suspended in the acid bath and given gentle agitation. Hydrochloric acid is generally used for crocodile skins together with salts and sometimes other acids. Pickled skin can be stored for months, especially if preservatives have been added to the pickling solution (Heidemann and Rother-Edward, 1993, Covington, 1997 and Mumford, 2010).

2.4.2   Tanning Operations

Tanning involves a complex combination of mechanical and chemical processes. The heart of the process is the tanning operation itself in which organic or inorganic materials become chemically bound to the protein structure of the hide and preserve it from deterioration. The substances generally used to accomplish the tanning process are chromium or extracts from bark of trees, such as chestnut. These tanning agents give rise to the two predominant types of tanning operations - chrome and vegetable tanning (Covington, 1997 and Turner, 2005).

2.4.2.1 Chrome Tanning

Most leather produced is chrome tanned. Chrome-tanned leather tends to be softer and more pliable than vegetable-tanned leather, has higher thermal stability, is very stable in water, and takes less time to produce than vegetable-tanned leather (Covington, 1997 and Turner, 2005).

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 retanning, dyeing, and fat-liquoring are usually performed to produce usable leathers and a preliminary degreasing step may be necessary when using animal skins, such as sheepskin (Mumford, 2010).

Chrome tanning in the United States is performed using a one-bath 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 into flesh and grain layers, and shaved to the desired thickness. The grain leathers from the shaving machine are then separated for retanning, dyeing, and fat-liquoring. Leather that is not subjected to scuffs and scratches can be dyed on the surface only. For other types of leather (that is, 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 (Covington, 1997 and Turner, 2005).

Fat-liquoring is the process of introducing oil into the skin before the leather is dried to replace the natural oils lost in beamhouse and tan-yard processes. Fat-liquoring is usually performed in a drum using an oil emulsion at temperatures of about 60 ^{0}C for 30 to 40 minutes. After fat-liquoring, the leather is wrung, set out, dried, and finished. The finishing process refers to all the steps that are carried out after drying (Mumford, 2010).

2.4.2.2 Vegetable Tanning

A tanning solution is prepared from bark, wood, fruits, pods or roots that contain tannin. 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 contains the 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 (Heidemann and Rother-Edward, 1993, Covington, 1997 and Mumford, 2010).

Tanning is essentially the reaction of collagen fibres in the hide with tannins, chromium, alum, or other chemical agents. The most common tanning agents are trivalent chromium and vegetable tannins extracted from specific tree barks. Other tanning agents include alum, syntans, formaldehyde, glutaraldehyde, and heavy oils (Heidemann and Roether-Eduard, 1993).

2.4.3 Post-Tanning Operations

Post-tanning operations comprise of re-chroming of semi-finished wet blue leather, neutralization, dyeing, fat liquoring and finishing. In case of post-tanning of vegetable tanned semi-finished leather, the operations involved are semi-chrome tanning, neutralization, dyeing, fat liquoring and finishing. However, the operations vary depending on the final product (Heidemann and Roether-Eduard, 1993).
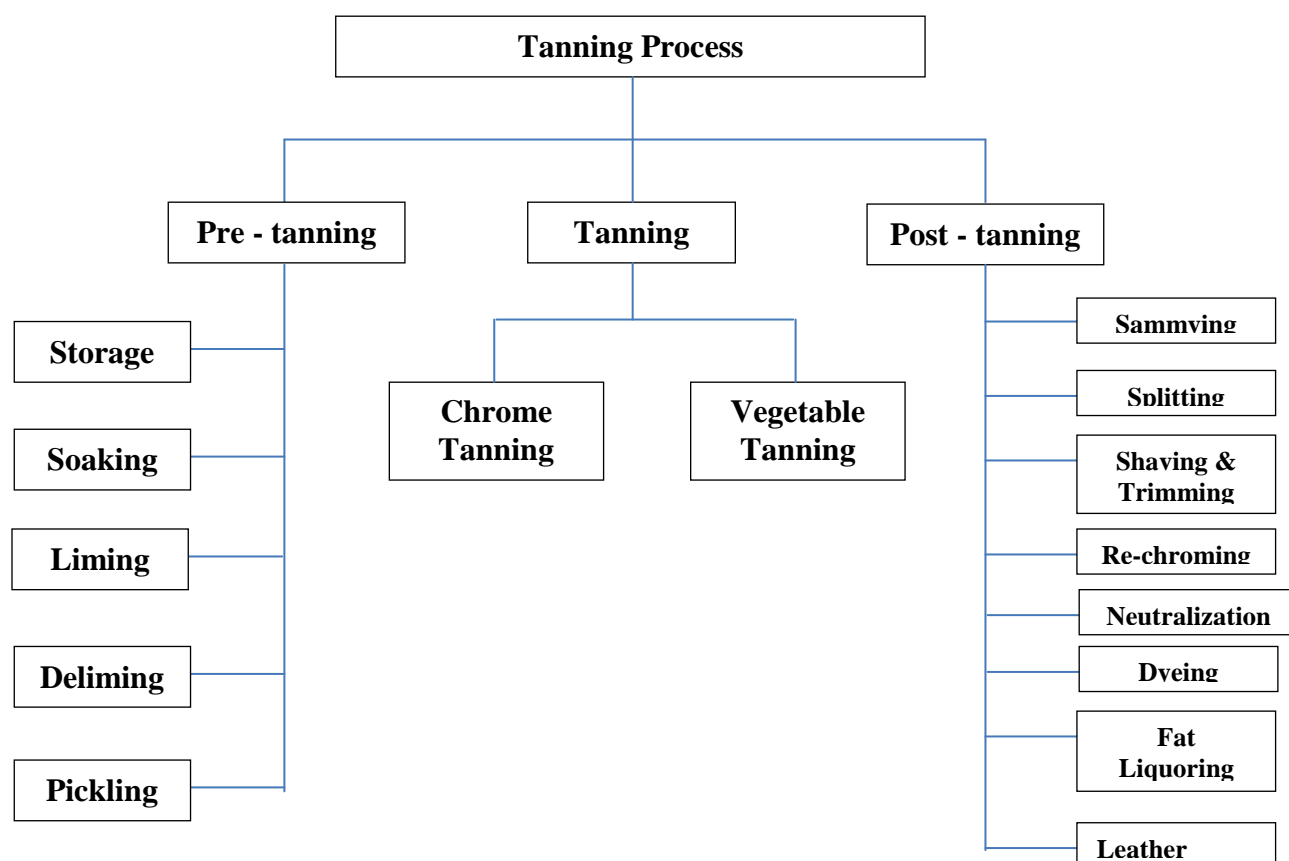
Figure 2. 1: The flow chart summary of tanning operations

(UNEP-UNIDO, 1991.Tanneries and the environment: A technical guide).

2.5 Chemicals used in tanning processes

Varieties of chemicals, from common salts (sodium chloride) to the fine finishing chemicals, are used in leather tanning. About 130 different types of chemicals are applied in leather manufacturing, depending on the type of raw material and the end product of

the industry. The chemicals consumed by tanneries involved in the Leather industry are listed in Table 2.2

Table 2. 1: Chemicals usually used in the entire tanning process(Wiemann et al., 1998)

High Potential Hazard Group					
Acetic acid	Ammonia	Calcium hydroxide	Formaldehyde	Formic acid	Glutaraldehyde hydrochloric acid
Hydrogen peroxide	Oxalic acid	Sodium chloride	Sodium hydroxide (Caustic soda)	Sulphuric acid	Sulphides and hydrosulphides
Moderate Potential Hazard Group					
Aluminium sulphate (as lacquer constituents)	Amyl alcohol (as lacquer constituents)	Benzyl alcohol (as lacquer solvent carbon black)	Chromium salts (trivalent) enzymes	Isopropyl perchloroethene toluene	White spirit
Low Potential Hazard Group					
Alums	Acetone	Albumen	Ammonium chloride	Ammonium sulphate	Borax, Boric acid
Casein	Calcium chloride	Castor oil	Ethanol (ethyl alcohol)	Fat liquors	Fats
Ferrous acetate	Ferrous sulphate	Gelatine	Glues	Lactic acid	Lanolines
Lecithin	Sodium bicarbonate	Paraffin	Pigment dispersions	Sequestering agents	Silicones
Sodium acetate	Oils	Sodium citrate	Sodium carbonate	Sodium formate	Sodium metabisulphate
Sodium nitrite	Sodium phthalate	Sodium sulphite	Sodium thiosulphate	Synthetic tannins	Tragacanth
Titanium salts	Vegetable tanning extracts	Waves	Wetting agents		

From the description of the tannery process in the previous section, it is obvious that a huge amount of resources such as water, raw hides and chemicals are used, but,

unfortunately only a small part of them can reach the final leather products, that is, large quantities come out as waste, posing threats to the environment.

2.6   Tanneries as a source of pollutants

Hides and skins pass through many liquors in the entire tanning process, each quite different in chemical composition and each playing its part in the conversion of unstable fibrous nature protein into a relatively stable non putrescible leather (Verheijen *et al*., 1996).

The wastewaters discharged by a tannery are the liquid wastes produced from each of the processes and the washing following each operation. While the spent liquors from each operation are dumped in batches, the washing from these operations are intermittently or continuously discharged, which causes a high fluctuation in the discharge of main stream (Verheijen *et al*., 1996).

Tanneries are typically characterized as pollution intensive industrial complexes, which generate widely varying, high-strength wastewaters. Variability of tannery wastewaters not only from the fill and from draw type operation associated with tanning processes, but also from the different procedures used for hide preparation, tanning and finishing. These procedures are dictated by the kind of raw hides employed and the required characteristics of the finished product (Bosnic *et al*., 2000).

Composite wastewater from a tannery is highly coloured and foul smelling. It is also alkaline with high amount of suspended and dissolved impurities. Among the most contaminated wastewater streams in the tanning process are the liming and tanning streams. Other streams are less contaminated when compared with liming and chrome

tanning streams since these two streams contain the two major toxic chemicals: sodium sulphide and chromium salts. This means that wastewater from tanneries should not be discharged directly into public sewerage systems before treatment processes (Wiemann *et al.,* 1998).

2.7   Major pollutants in tannery wastewaters

2.7.1   Solids

The solids to be found in tannery effluent fall into several distinct categories.

2.7.1.1 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. They are made up of solids with two different characteristics.

Solids with a rapid settling rate (settleable solids) are solids which comprise of material that can be seen in suspension when an effluent sample is shaken, but settle when the sample is left to stand. 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 (tanning) processes. Even a thin layer of settled sludge can form a blanket that deprives sections of the river or lake bed of oxygen. Plant and aquatic life dies and decomposition sets in (Bosnic *et al*., 2000).

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.

They can, however, be filtered from solutions. Together with the more readily settleable solids, they thus comprise the suspended solids of an effluent that can be measured analytically.

Most of these solids are protein residues from the beam-house operations – mainly liming processes. Large quantities are also produced owing to poor uptake in vegetable tanning processes and 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 (Kurt *et al*., 2007).

2.7.1.2 Gross solids

Gross solids are larger than what a sampling machine can handle, hence they are not measured. Their presence, however, is clear to see and the dangers they pose are fully recognized. The waste components that give rise to this problem are often large pieces of leather cuttings, trimmings and gross shavings, fleshing residues, solid hair debris and remnants of paper bags. They can be easily removed by means of coarse bar screens set in the waste water flow. If, however, they emerge from the factory, they settle out very rapidly (Bosnic *et al*., 2000).

2.7.2 Oxygen demand

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 balance maintained in the water becomes overloaded. Oxygen is stripped from the water causing oxygen dependent

plants, bacteria, fish as well as the river or stream itself to die. The outcome is an environment populated by non-oxygen dependent (anaerobic) bacteria leading to toxic water conditions (Verheijen *et al*., 1996).

A healthy river can tolerate substances with low levels of oxygen demand. The load created by tanneries, however, is often excessive, and the effluent requires treatment prior to discharge. This is often achieved by using bacteria in a properly operated effluent treatment plant: a process demanding high levels of oxygen. Oxygen induction can be achieved by blowing large volumes of air into the effluent: a process entailing a high-energy demand and, as a corollary, high capital and operational costs. In order to assess an effluent's impact on discharge to surface waters or determine the costs of treatment, the oxygen demand needs to be determined. This can be achieved in two different ways.

2.7.2.1 Biochemical oxygen demand (BOD)

Biochemical oxygen demand is the amount of dissolved oxygen needed by aerobic biological organisms in a body of water to break down organic material present in a given water sample at certain temperature over a specific time period. The term also refers to a chemical procedure for determining this amount. This is not a precise quantitative test, although it is widely used as an indication of the organic quality of water (Verheijen *et al*., 1996).

The technique for measuring BOD is complex. Essentially, the effluent sample once shaken is left to stand for one hour so that all settleable solids are excluded from the analysis. The liquor above the precipitate (supernatant) is drawn off and used in the analysis. A suitable volume of this sample is diluted in water, pH adjusted, and seeded

with bacteria (often settled sewage effluent). The samples are then incubated in the dark for five days at 20 ^{0}C. The oxygen dissolved in the water is used by the bacteria while over time the organic matter in the sample is broken down. The oxygen remaining is determined either by means of an oxygen meter or by analysis. The level of oxygen demanded by the effluent can be calculated by comparison to the blank effluent-free samples (Wiemann *et al*., 1998).

The BOD analysis is widely used to assess the environmental demands of waste water. This method of detection has various weaknesses: the bacterial cultures can vary and the analysis is a highly sensitive process. If the most stringent care is not taken during the preparation and the analysis itself, the results can be misleading (Mollah *et al*., 2001).

It should also be remembered that although BOD is a measure of the oxygen requirements of bacteria under controlled conditions, many effluent components take longer than the period of analysis 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 the chemicals used in manufacturing leathers, including certain retanning agents, some synthetic fat liquors, dyes and residual proteins from hair solubilisation (UNIDO, 2000).

2.7.2.2 Chemical oxygen demand (COD)

The chemical oxygen demand test is commonly used to indirectly measure the amount of organic compounds in water. Most applications of COD determine the amount of organic pollutants found in surface water (for instance, lakes and rivers) or wastewater, making

COD a useful measure of water quality. It is expressed in milligrams per litre (mg/L) also referred to as ppm (parts per million), which indicates the mass of oxygen consumed per Litre of solution (Verheijen *et al*., 1996).

This method measures 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 long-term biodegradable products, as well as the chemicals that remain unaffected by bacterial activity.

The method is very aggressive. A suitable volume of effluent is boiled with a powerful oxidizing agent (potassium dichromate) and sulphuric acid. As the effluent components oxidize, they use oxygen from the potassium dichromate; the amount used being determined by titration (Verheijen *et al*., 1996). This method is often favoured as it provides rapid results (hours as opposed to days). It is more reliable and cost effective as it is easier to manage larger numbers of samples (Bosnic *et al*., 2000).

The results are always higher than those obtained using the BOD analysis. As a rule of thumb, the ratio between COD: BOD is 2.5:1, although in untreated effluent samples variations can be found as great as 2:1 and 3:1. This depends on the chemicals used in the different leather making processes and their rate of biodegradability (Kurt *et al*., 2007).

2.7.3 Nitrogen

Nitrogen is contained in several different components in tannery effluent. Sometimes these sources have to be differentiated. 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) (Bosnic *et al*., 2000).

These sources of nitrogen pose two direct problems.

1. Plants require nitrogen in order to grow, but the high levels released by substances containing nitrogen over-stimulate growth. Water-based plants and algae grow too rapidly, where upon water ways become clogged and flows are impaired. As the plants die, a disproportionately high amount of organic matter has to be broken down. If the load outstrips the natural supply of oxygen from the river, plants, fish and aerobic bacteria die and ultimately anaerobic conditions develop.

2. The nitrogen released through protein break down and the deliming process is in the form of ammonia. The latter can be converted by bacteria over several stages into water and nitrogen gas which is ultimately released into the atmosphere. Both of these breakdown products are non-toxic, yet large volumes of oxygen are needed in the process. If oxygen demand is greater than the level supplied naturally by the water course, toxic anaerobic conditions can rapidly develop.

The nitrogenous compounds can be broken down by combining intensive aerobic and anaerobic biological treatment. The oxygen demand is very high, thus leading to correspondingly high operational and energy costs. Calculations show that with typical tannery effluent, some 40% of the oxygen requirements are spent on removing the nitrogen component (Bosnic *et al*., 2000).

The compounds containing nitrogen can be determined by the Kjeldahl method of analysis. In this technique, all the nitrogenous matter is digested on being boiled with

sulphuric acid to form ammonium compounds. In a second stage, the ammonia is released on being boiled with sodium hydroxide, and subsequently trapped in a boric acid solution. The level of ammonia released is determined by titration, and its value calculated as nitrogen (Bosnic *et al*., 2000).

2.7.4 Sulphide (S^{2-})

The sulphide content in tannery effluent results from the use of sodium sulphide and sodium hydrosulphide, and the breakdown of hair in the unhairing process (Wiemann *et al.,* 1998). The sulphides pose many problems: under alkaline conditions, sulphides remain largely in solution. When the pH of the effluent drops below 9.5, hydrogen sulphide evolves from the effluent: the lower the pH, the higher the rate of evolution. The gas is characterized by a smell of rotten eggs, a severe odour problem occurs.

Comparable in toxicity to hydrogen cyanide, even a low level of exposure to the gas induces headaches and nausea, as well as possible damage to the eye. At higher levels, death can rapidly set in and countless deaths attributable to the build-up of sulphide in sewage systems have been recorded (Wiemann *et al*., 1998).

Hydrogen sulphide gas is also fairly soluble. When absorbed, weak acids can form and cause corrosion. This weakens metal roofing, girders and building supports. In sewers, major problems can arise as metal fittings, structural reinforcements and pipe-work corrode. If discharged to surface water, even low concentrations pose toxicological hazards. Sulphides can be oxidized into non-toxic compounds by certain bacteria in rivers; however, this creates oxygen demand which, if excessive, can harm aquatic life (Wiemann *et al*., 1998; Bosnic *et al*., 2000).

Sulphides in effluent can be determined in several ways. One of the most accurate methods relies on the acidification of suitable quantities of effluent to generate hydrogen sulphide. This is flushed through the apparatus using nitrogen gas, where after it is trapped and converted into zinc sulphide. The amount of sulphide is determined by titration (Wiemann *et al*., 1998).

2.7.5 Neutral salts

There are two common types of salts found in tannery effluent.

2.7.5.1 Sulphates (SO_4^{2-})

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 (Wiemann *et al*., 1998).

Problems arise with soluble sulphates, however, for two main reasons:

1. Sulphates cannot be removed completely from a solution by chemical means. Under certain biological conditions, it is possible to remove the sulphate from a solution and bind the sulphur into microorganisms. Generally, however, the sulphate either remains as sulphate or is broken down by anaerobic bacteria to produce malodorous hydrogen sulphide. This process occurs very rapidly in effluent treatment plants, sewage systems and water courses, if effluents remain static. This bacterial conversion to hydrogen sulphide in sewage systems results in the gradual corrosion of metal parts.

2. If no breakdown occurs, the risk of increasing the total concentration of salts in the surface water and groundwater runs is incurred.

Sulphate analysis is performed by adding barium chloride solution to a sample of filtered effluent. The sulphates are precipitated as barium sulphate and filtered; drying and calculation can determine the sulphate level.

2.7.6 pH value

Acceptable limits for the discharge of waste waters to both surface waters and sewers vary, ranging 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 of life (Wiemann *et al*., 1998).

Municipal and common treatment plants prefer discharges to be more alkaline as it reduces the corrosive effect on concrete. Metals tend to remain insoluble and more inert, and hydrogen sulphide evolution is minimized. When biological processes are included as part of the treatment, the pH is lowered to more neutral conditions and carbon dioxide is evolved (Chandra *et al*., 2008).

2.7.7 Chromium compounds

Metal compounds are not biodegradable. They can thus be regarded as long term environmental features. Since they can also have accumulative properties, they are the subjects of close attention. Two forms of chrome are associated with the tanning industry, whose properties are often confused (Bosnic *et al*., 2000 and Chandra *et al*., 2008).

2.7.7.1 Chrome +III (trivalent chrome, chrome III)

Chromium is mainly found in waste from the chrome tanning process; it occurs as part of the retanning system and is displaced from leathers during retanning and dyeing processes. This chrome is discharged from processes in soluble form; however, when mixed with tannery waste waters from other processes (especially if proteins are present), the reaction is very rapid. Precipitates are formed, mainly protein-chrome, which add to sludge generation (Verheijen *et al*., 1996).

However, very fine colloids are also formed which are then stabilized by the chrome - in effect, the protein has been partially tanned. The components are thus highly resistant to biological breakdown, and the biological process in both surface waters and treatment plants is inhibited.

Once successfully broken down, chromium hydroxide precipitates and persists in the ecosystem for an extended period of time (Bosnic *et al*., 2000 and Chandra *et al*., 2008).

If chrome discharges are excessive, the chromium might remain in the solution. Even in low concentrations, it has a toxic effect upon daphnia, thus disrupting the food chain for fish life and possibly inhibiting photosynthesis (Bosnic *et al*., 2000).

Chrome levels can be determined in a number of ways. The first stage, however, usually comprises boiling a known volume of sample with concentrated nitric acid to ensure complete solution of the chrome. After suitable dilution, the chromium level is determined by atomic absorption. Where high levels of chrome are expected, iodine/thiosulphate titrations are sometimes used. That technique, however, is inaccurate at low concentrations (Muchangi, 2012)

2.7.7.2 Hexavalent chrome, chrome VI

Tannery effluents are unlikely to contain chromium in this form. Dichromates are toxic to fish life since they swiftly penetrate cell walls. They are mainly absorbed through the gills and the effect is accumulative. Analysis is highly specialized. The concentrations normally anticipated are very low and analysis is based on colorimetric measurement at 670 nm (Bosnic *et al*., 2000).

2.7.8 Other metals

Other metals which might be discharged from tanneries and whose discharge may be subject to statutory limits include Al, Zn, Pb, Ni and Fe. Depending on the chemical species, these metals have differing toxicities that are also affected by the presence of other organic matter, complexing agents and the pH of the water (Connell and Miller, 1984).

2.7.9   Solvents

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 (Bosnic *et al*., 2000).

2.8 Tannery effluents treatment

As discussed above, manufacturing of leather, leather goods produces various harmful chemical and physical pollutants (IPAR, 2004). Consequently, the uncontrolled release of tannery effluents to natural water bodies increases health risks for human beings and environmental pollution. To avert these perilous effects, tannery wastes should be treated

before being dumped into water bodies and to the environment. Tannaries wastewater/effluents can be treated in many different ways in order to avoid the wide range of toxic effects on the environment caused by untreated tannery effluents and sledges.

The following are the main phases of tannery wastewater treatment:

   i.   Mechanical treatment

  ii.   Effluent treatment

 iii.   Post-purification, sedimentation and sludge handling

2.8.1   Mechanical Treatment

This is usually the first treatment of the raw effluent. It includes screening to remove coarse material. Up to 30-40% of gross suspended solids in the raw waste stream can be removed by properly designed screens. Mechanical treatment may also include skimming of fats, grease, oils, and gravity settling. Coagulation and flocculation are also part of this treatment to remove a substantial percentage of the COD and suspended solids (Mollah *et al*., 2001).

After mechanical treatment, physico-chemical treatment is usually carried out, which involves the chrome precipitation and sulphide treatment. Effluent from tanneries after mechanical and physico-chemical treatment is generally easily biodegradable in standard aerobic biological treatment plants (Mollah *et al*., 2001).

2.8.2   Effluent treatment

In this case, flow segregation is used to allow preliminary treatment of concentrated wastewater streams, in particular for sulphide and chrome-containing liquors. Although a

reduction of water consumption does not reduce the load of many pollutants, concentrated effluents are often easier and more efficient to treat (Favazzi, 2002). Where segregation of flows is possible, thorough mixing of chrome-bearing effluents and other effluent streams improves the efficiency of the effluent treatment plant because the chromium tends to precipitate out with the protein during pretreatment (Huang, 2002).

It is common practice to keep sulphide-containing effluent from the beam-house separate and at a high pH until the sulphide is treated, because at a pH lower than 9, the formation of toxic H_2S gas can occur. The sulphides in the deliming and pickle liquors can easily be oxidized in the drum by adding hydrogen peroxide, sodium metabisulphite or sodium bisulphite. The associated emission level after treatment of sulphide is 2 mg/L in a random sample in the separate effluent.

Where segregation of sulphide-bearing liquors is not possible, the sulphides are generally removed by means of precipitation with iron (II) salts and aeration. A disadvantage of this precipitation is the generation of high volumes of sludge (Mollah *et al*., 2001).

2.9 Related studies

Studies in Chile on the evaluation of waste water quality based on chemical specific measurements and toxicity tests reveal that toxicity of a beamhouse effluent after an activated sludge reactor treatment of effluent from different tannery processes (soaking, beamhouse and tanning) demonstrated high values of COD, sulphate and total solids. All effluents showed extremely toxic effects (Cooman *et al*., 2003). A great deal of these effluents has been continuously discharged in soils. It is known that heavy metals added to soils are rapidly and specifically adsorbed by the solid fraction. However, their

availability, potential toxicity and mobility within the soil profile will depend upon the binding forms with clays, organic matter and hydrous oxides, oxides and oxyhydroxides. The interactions of their associations with time; the saturation of specific sites of adsorption; the crystallinity and morphology of absorbent surfaces; pH variation10-13 and physicochemical characteristics (Khan and Anjaneyulub, 2005).

Several studies on tannery effluents have shown that the availability of Cr(III) in the soil solution is limited by the formation of hydroxides as $Cr(OH)_3$ and $Cr_2O_3(H_2O)$, at pHs, 6-12, or by co-precipitation with Fe, forming $(Cr_x,Fe_{1-x})(OH)_3$, $(Cr_x,Fe_{1-x})OOH$, $Fe_x,Cr_{2x}O_3$ leading to increase in COD (Stepniewska *et al.,* 2004). Studies conducted in India show levels of Pb varying from 6-10 mg/L whereas those of Cr vary from 800-1400 mg/L. A similar trend has been shown by results from Egypt that revealed Cr levels varying from 600-1300 mg/L while those of Pb being 5-10 mg/L (Cooman *et al*., 2003; Khan and Anjaneyulub, 2005).

By applying industrially proven low-waste advanced methods such as the use of salt-free preserved raw hides and skins, hair-save liming, low-ammonia or ammonia-free deliming and bating, advanced chrome management systems, it is possible to decrease significantly the pollution load, namely: COD and BOD_5 by more than 30%, sulphides by 80-90%, ammonia nitrogen by 80%, total (Kjeldahl) nitrogen by 50%, sulphates by 65%, and chromium by up to 90% (Akan *et al*., 2009). The chemical parameters such as COD, BOD, nitrite, sulphur and chromium, were found to be much above the permissible limits prescribed by the Bureau of Indian Standards and tanneries` pollution readily accelerates to cause deterioration in ground water quality (Akan *et al*., 2009). A number of investigations reported on BOD in tannery effluent in Malawi reveal variations between

2906- 9000 mg/L whereas, in the neighbouring country Zambia, similar values are observed ranging between 2800-12000 mg/L (Tamilchelvan and Dhinakaran, 2012).

Effluents of six different leather industries of Bara and Parsa districts (Nepal) discharging their effluents into Sirsiya River were analyzed. The amounts of chromium present in effluents of leather industries and the river water were found to lie between 0.12 -345.00 mg/L (0.12 mg/L) (Shukla *et al.*, 2006). Effluents from tanneries in India show Fe discharges ranging between 5.45-7.52 mg/L while similar studies in New York reveal Fe values ranging from 1.65 – 1.74 mg/L (Bhatia, 2005). Whereas studies in New York reveal no traces of Pb in their tannery effluent, studies in India show traces of this element ranging from 1.5-3.8 mg/L which is far beyond the requirements of the environmental protection agency (0.05-0.5 mg/L) of the area under study (Bhatia, 2005).

The mean DO concentrations of effluent in some Indian tannery industries for rainy season ranged between 27.33 to 38.22 mg/L and 1.76 mg/L for dry season, these variations could be due to chemicals used in tannaries which increase the organic matter leading to low DO values. Despite these variations in DO between industries, there were no marked or distinct variations for DO between seasons, indicating that the activities of these industries remain almost constant throughout the seasons. The higher levels of BOD in the rainy and dry seasons were 672.70 and 664.30 mg/L, respectively (Bhatia, 2005).

Chromium metal was, however, found to be 89.30% higher, against the lower value of 0.255 mg/L reported for textile industries effluent in Lagos metropolis. Whereas in tannery industry effluent, chromium (VI) level was found to be 7.21 mg/L, which was

9.89% lower as compared to the value of 9.0 mg/L reported for tannery effluent (Shukla *et al*., 2006). Chromium can cause allergic reactions in the skin, damage the lungs and asthma attacks. Studies in Challawa Tannery in Kano State reveal that concentrations of Fe vary between (1.23- 4.01 mg L^{-1}) while studies in levels of chromium showed a variance of (1.56 to 4.13 mg L^{-1}) (Matsuo *et al*., 2001).

Studies in Indonesia during the dry season show that, the values of Pb were below the detectable level and an average value of this element was reported as 0.06 mg/L in tannery effluent. In excess amount, Pb affects central nervous system, particularly in children and also damages kidneys and the immune system (Kaushik, 2003 and Tariq *et al*., 2006).

 Related studies in Argentina (Cooman *et al*., 2003) reveal that the pH values of tannery effluent range between 4.5-7.5, tannery effluents in Kanpur (Tariq *et al*., 2006) show pH variables ranging from 3.7-5.9, while further studies in Nepal give pH values ranging from 1-6 (Kaushik, 2003).

Total suspended solids(TSS) have become a major problem in many countries. For example, South Africa research results (Bosnic *et al*., 2000) show TSS values range between 250-750 mg/L, Italy (Kurt *et al.,* 2007) has values varying between 200-800 mg/L while studies in India reveal that TSS values vary between 310 - 900 mg/L (IUE 2001).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

The map below shows the location of the tannery and the sampling points.

Legend

S1	Pretanning
S2	Tanning
S3	Post tanning
S4	Discharge to the river
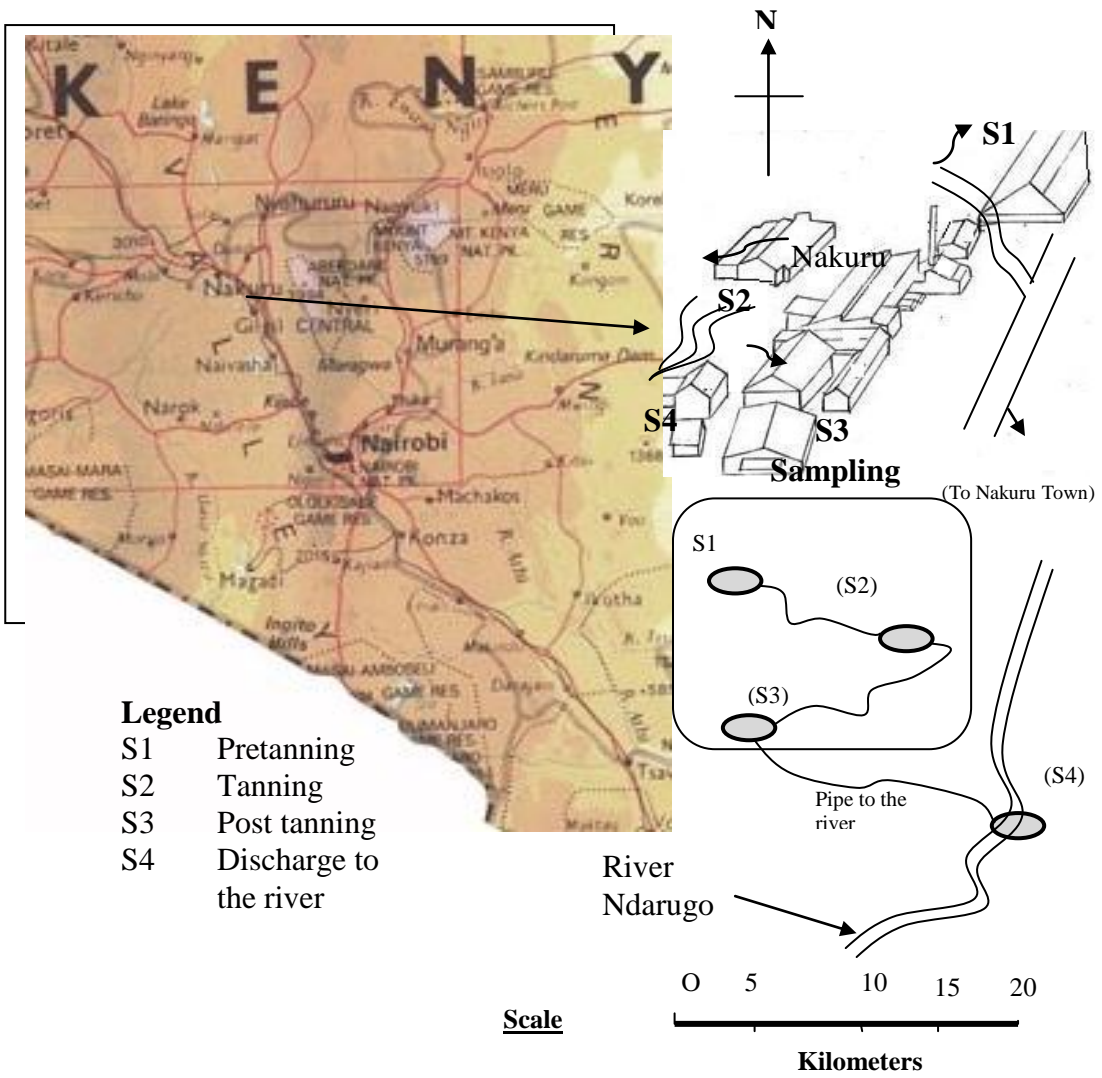
Figure 3.1: Map of the Study Area (Source: Author, 2013).

Wastewater Sampling

The effluent samples were collected from four strategic sites in the tannery and the surrounding area. The first sampling point was the pre-tanning stage where effluents are released after all the soaking, liming and de-liming processes. A 500 mL sample was collected from this point and denoted S1 located immediately after the tanning process just before the screens.

The second sampling point of collection was the tanning stages that is, the effluents after the chrome and vegetable tanning. A 500 mL sample was collected from this point and denoted S2.

The third sampling point was the post-tanning/finishing stage just before the water is pumped to the river. A 500 mL sample was collected from this point and denoted S3. The final sampling point was the public sewer where the wastewater is dumped. A 500 mL sample was collected from this point and denoted S4.

Containers of 500 mL were used for sampling. Samples were collected in autoclaved reagent glass bottles and immediately stored in ice before being transported to the laboratories of University of Eldoret.

3.2 Sample preservation

After collection, the samples were transported to the chemistry laboratory of the University of Eldoret for refrigeration at 4 $^{\circ}$C mainly to inhibit biological activity of samples. Where some were analysed for while others were also taken to Eldoret water sanitation company for analysis.

3.3 Experimental Procedures

3.3.1   BOD and OD Analysis

Since samples for BOD analysis may change greatly during handling and storage, testing was done immediately after collection. Chlorine being a strong oxidizing agent, it inhibits the growth of living bacteria in the BOD test; hence samples were pretreated to remove chlorine before the BOD test was run. This was done by adding sodium sulphite to the samples. A 100 mL portion of each sample was pipetted into BOD bottles of 500 ml containing aerated dilution water. The DO content was determined and recorded and then the bottles were incubated in the dark for five days at 20 °C. At the end of five days, the final DO contents were determined and the difference between the final DO reading and the initial DO reading were calculated for each sample. The decrease in DO reading for each sample was collected for sample dilution, and the difference represents the BOD of the sample.

For each test bottle meeting the 2.0 mg/L minimum DO depletion and the 1.0 mg/L residual DO, BOD was calculated as follows (APHA, 1995):

When dilution water is not seeded:

$$\text{BOD, mg/L} = \frac{D_1 - D_2}{P}$$

When dilution water is seeded:

$$\text{BOD, mg/L} = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P}$$

Where:

D_1 = DO of diluted sample immediately after preparation, mg/L,

D_2 = DO of diluted sample after 5 days incubation at 20°C, mg/L,

P = decimal volumetric fraction of sample used,

B_1 = DO of seed control before incubation, mg/L,

B_2 = DO of seed control after incubation mg/L, and

f = (volume of seed in diluted sample)/ (volume of seed in seed control)

3.3.2 COD Analysis

In this case, the samples, standards, and blanks were heated at 150 ^{0}C in a closed reactor for two hours in the presence of acid dichromate solution. The samples were oxidized by digesting in sealed reaction tubes with sulphuric acid and potassium dichromate in the presence of silver sulphate catalyst. The amount of dichromate reduced was proportional to the COD of each sample. A reagent blank was prepared prior to each batch of tubes in order to compensate for the oxygen demand of the reagent itself.

Over the range of the test, a series of colours from yellow through green to blue were produced. The colours were indicative of the COD of each sample and were measured using a photometer. The results were expressed as milligrams of oxygen consumed per Litre of each sample.

3.3.3 Determination of TSS

The filters were washed using distilled H_2O and dripped prior to the analysis. The pre-washed and prepped filters were weighed and the weight recorded. Each sample was slowly filtered to completion. After the completion of the filtration process, the filter papers were carefully removed from filtration apparatus using forceps and transferred to a glass weighing dish as a support and dried for 1 hour at 110 °C in drying oven.

After drying was complete in the oven, the filters were reweighed and the weights recorded. The TSS was calculated as follows:

$$TSS\left(\frac{mg}{L}\right) = \frac{(Residue + Filter)(mg) - Filter(mg)}{Sample\ filtered\ (mL)} \times 1000\left(\frac{mL}{L}\right)$$

3.3.4 Determination of pH

pH of the individual samples were measured immediately after collection. The determination of the pH values of the samples was done using the pH meter by following the standard procedure.

3.3.5 Measurement of temperature of samples at collection points

The temperatures of the surface waters at the sampling points were measured by using the conventional mercury thermometer by dipping the thermometer for about a minute. The temperatures were then recorded appropriately.

3.3.6 Determination of turbidity

Turbidity level of each of the four samples was determined using turbidometer tube. In this case, each wastewater sample was stirred thoroughly in order to disperse the solids and to eliminate any trapped air bubbles. Each sample was then poured into the turbidometer tube and turbidity read directly from the instrument scale and recorded appropriately.

3.3.7 Determination of total phosphorus

This was done using a UV-Vis spectrometer (model DR 200). In this case, 50 mL of each sample was transferred into a clean Erlenmeyer flask and 1 mL of conc. sulphuric acid added.

A 0.40 g ammonium per sulphate was added and then the mixture was boiled gently until a final volume of about 10 mL was reached. The mixture was then cooled and diluted approximately to 40 mL then filtered. The total phosphorus in each sample was then determined by measuring the absorbance at 650 nm with flame atomic absorption spectrophotometer model and then determining the phosphorus concentration from the standard curve.

3.3.8   Determination of total Cr

A 100 mL portion of each sample was taken, filtered through Whatman 42 filter paper and then acidified with concentrated HNO_3 to bring down the pH up to 2.0. A 100 mL of sample was taken and 5 ml concentrated HNO_3 added. The mixture was digested in a closed chamber for 30 minutes then the volume made up to 100 mL with distilled water.

The Cr (VI) concentrations in samples were determined colorimetrically by using flame atomic absorption spectrophotometer at 540 nm by diphenylcarbazide (DPC) method.

3.3.9   Determination of total sulphates

This was done by acidifying a 10 mL portion of each sample with HCl and then $BaSO_4$ added to the sample in order to precipitate sulphates as BaCl. After a period of digestion, the precipitate was filtered off and washed thoroughly with water in order to remove all the chlorides. The precipitate was then ignited and weighed as $BaSO_4$. The amount of sulphate was then easily calculated using the equation:

$$\frac{mg}{L}(SO_4^{2-}) = \frac{mg\ BaSO_4\ x\ 411.5}{mL\ of\ the\ sample}$$

3.3.10 Determination of Pb

A 10 mL portion of each sample was taken, filtered through Whatman 42 filter paper and then acidified with concentrated HNO_3 to bring down the pH up to 2.0. A 5 mL of conc. HNO_3 were added to 100 mL of each sample and then the mixture digested in a closed chamber for 30 minutes after which the solution was made up to 100 mL with distilled water. Digested samples were analyzed for Pb concentrations by flame atomic absorption spectrophotometer.

3.3.11 Determination of Fe

10 mL portion of each sample was taken, filtered through Whatman 42 filter paper and then acidified with concentrated HNO_3 to bring down the pH up to 2.0. Approximately 5 mL of conc. HNO_3 was added to 100 mL of each sample and then the mixture digested in a closed chamber for 30 minutes after which the solution was made up to 100 mL with distilled water.

Flame atomic absorption spectrometer equipped with hollow cathode lamps was used for the determination of Fe in the four waste water samples. The photometric measurements were carried out at a wavelength of 510 nm.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1   Introduction of Results

Although tannery wastewater analytical tests are often separated into categories, it is important to understand that these tests are not independent of each other as shown by figure 3. In other words, a contaminant identified by one test in one category can also be identified in another test in a separate category. For example, the organics in a tannery wastewater sample represented by BOD will also be represented in the spectrum of solids, as TSS.
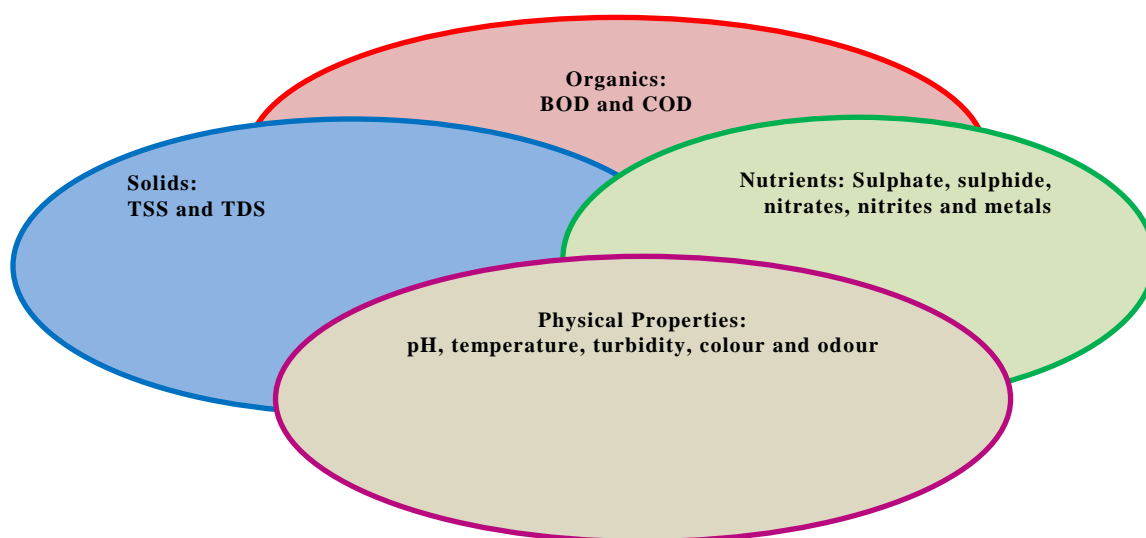
Figure 4. 1: Spectrum of solids, Organics, Physical Properties and Nutrients

In this study there were grand differences between the parameters of the four different samples collected in different parts of the tannery. This could be mainly attributed to the different chemicals and temperature conditions involved in each section of the tanning process.

For analytical purposes, samples were divided into four main categories in reference to the four consecutive sampling points:

(a) Samples from effluents of the preparatory processes:

This included soaks, limes, dehairing liquors, bates and pickles, deliming liquors, and all kinds of washings. Soaks are heavily charged with conservation means and organic matters. Limes are loaded with suspended matters, strongly alkaline due to the excess of lime and contain the main amount of sulphide. Dehairing liquors contain sulphides as well and organic compounds in dissolved or colloidal form. Bates contain protolytic enzymes and smaller concentrations of calcium salts. Pickles have a slightly acid reaction.

(b) Samples from effluents of the tanning processes:

This group comprised of effluents from chrome and vegetable tanning sections. Two basic tanning processes are used at present in modern manufacture: chrome and vegetable tanning. Effluents from chrome tanning contain trivalent chromium compounds. Effluents from vegetable tanning are loaded with vegetable tanning materials, especially of the pyrogallol and catechol groups. At present, these are replaced by synthetic materials.

(c) Sample from effluents of the final processes:

This group is represented by the wastes from neutralization, dyeing and fat-liquoring. These effluents contain organic and inorganic acids, dyestuffs, chromium salts and fats.

(d) Samples from the dumping site:

This group represents the waste waters at the final dumping site where the effluents of the entire tanning process are dumped. Little decontamination is performed to the effluents before dumping is done. After this stage, the effluents are washed into river Ndarugo from which water is widely used for domestic purposes such as irrigation, drinking water, bathing and washing clothes.

4.2 Results

Table 4.1: Results obtained from the analysis of the four samples from Nakuru

tannery

Parameters	Sampling stations	Mean measurements	± S.E	Parameters	Sampling stations	Mean measurements	± S.E
Temp (^{0}C)	S1	24	0.577	Pb (mg/L)	S1	5.5	0.577
	S2	22.1	0.577		S2	6.5	0.0577
	S3	24.62	0.566		S3	4.5	0.115
	S4	23.413	0.31		S4	4	0.0115
DO (mg/L)	S1	0.3	0.029	Fe (mg/L)	S1	2.6	0.0577
	S2	0.8	0.058		S2	4.6	0.115
	S3	1.51	0.058		S3	5.4	0.0577
	S4	1.39	0.058		S4	4.4	0.0577
COD (mg/L)	S1	6000	11.5	NO_3^- (mg/L)	S1	39.4	0.0577
	S2	9107	4.04		S2	50	0.0577
	S3	8145	5.77		S3	83.3	0.0577
	S4	7930	2.89		S4	85.2	0.115
BOD (mg/L)	S1	1369	5.77	NO_2^- (mg/L)	S1	120.44	0.0635
	S2	9150	5.77		S2	133.35	0.0115
	S3	8000	5.77		S3	143.53	0.0173
	S4	7700	5.77		S4	146.7	0.115
TSS (mg/L)	S1	294.4	2.31	PO_4^{3-} (mg/L)	S1	10.29	0.00577
	S2	224.6	0.577		S2	9.71	0.0173
	S3	158.25	0.577		S3	12.4	0.0577
	S4	214.3	0.577		S4	11.1	0.0577
SO_4^{2-} (mg/L)	S1	318.5	0.577	EC (μS/cm^2)	S1	14550	5.77
	S2	267	0.577		S2	14670	5.77
	S3	214.5	0.577		S3	14720	11.5
	S4	212.1	0.577		S4	14620	5.77
Cr (mg/L)	S1	0	0	Turbidity (NTU)	S1/S2/S3/S4	>1000	

	S2	945	1.73	pH	S1	24	5.66
	S3	700	5.77		S2	22	7.20
	S4	680	5.77		S3	24.62	5.77
					S4	22.8	7.00

Table 4.2: Maximum NEMA and WHO permissible values in waste water

PARAMETER	WHO	NEMA
pH	5.5 – 8.5	5.5 – 9.0
Temperature (^{0}C)	40	20 – 35
TSS (mg/L)	150	100
Electrical Conductivity (μScm^{-2})	400	400
Turbidity (NTU)	350	300
Pb (mg/L)	0.05	0.1
NO_3^- (mg/L)	100	100
BOD (mg/L)	100 – 300	100 – 300
Fe (mg/L)	300	300
COD (mg/L)	260	250
BOD (mg/L)	350	360
NO_2^- (mg/L)	50	50
TDS (mg/L)	600	500
SO_4^{2-} and S^{2-} (mg/L)	15	18
Cr mg/L	0.5	0.05
Phosphate (PO_4) mg/L	30	30

Table 4.3: Analysis of Variance

Analysis of Variance for EC (µS/cm-2), using Adjusted SS for Tests					
Source	DF	SeqSS	Adj SS	Adj MS	F	P
Sample	3	47400	47400	15800	90.29	0
Error	8	1400	1400	175		
Total	11	48800				

Analysis of Variance for Pb (mg/L), using Adjusted SS for Tests					
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sample	3	11.0625	11.0625	3.6875	14.04	0
Error	8	2.1008	2.1008	0.2626		
Total	11	13.1633				

Analysis of Variance for BOD (mg/L), using Adjusted SS for Tests					
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sample	3	111083012	111083012	37027671	370276.7	0
Error	8	800	800	100		
Total	11	111083812				

Analysis of Variance for COD (mg/L), using Adjusted SS for Tests					
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sample	3	15252279	15252279	5084093	35429.22	0
Error	8	1148	1148	143		
Total	11	15253427				

Analysis of Variance for pH, using Adjusted SS for Tests					
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sample	3	87.27	87.27	29.09	38.28	0
Error	8	6.08	6.08	0.76		
Total	11	93.35				

Analysis of Variance for Temp (^{0}C), using Adjusted SS for Tests					
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sample	3	10.4024	10.4024	3.4675	4.27	0.045
Error	8	6.4979	6.4979	0.8122		
Total	11	16.9003				

Analysis of Variance for DO (mg/L), using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sample	3	2.82660	2.82660	0.94220	115.96	0.000
Error	8	0.06500	0.06500	0.00813		
Total	11	2.89160				

Analysis of Variance for Cr (mg/L), using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sample	3	1482056	1482056	494019	9454.90	0.000
Error	8	418	418	52		
Total	11	1482474				

Analysis of Variance for Fe (mg/L), using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sample	3	12.5700	12.5700	4.1900	239.43	0.000
Error	8	0.1400	0.1400	0.0175		
Total	11	12.7100				

Analysis of Variance for TSS (mg/L), using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sample	3	28106.2	28106.2	9368.7	1972.36	0.000
Error	8	38.0	38.0	4.8		
Total	11	28144.2				

Analysis of Variance for SO_4^{2-} (mg/L), using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Sample	3	22923.9	22923.9	7641.3	7641.31	0.000
Error	8	8.0	8.0	1.0		
Total	11	22931.9				

The effluent released from Nakuru tannery industry was brown in colour and had an offensive odour. The colour of this effluent could be due to the presence of biodegradable and non-biodegradable high molecular weight organic compounds and high amount of chemicals used during the processing while the odour could be due to the processing of skin and hides by soaking and liming. The yellowish brown colour could be hindering the penetration of sunlight causing depletion in the rate of oxidation process.

Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted with no change in direction or flux level through the sample. The turbidity of the four effluent samples was greater than 1000 NTU. This could be attributed to the different chemicals and suspended solids in the effluents resulting from the processes in the pre-tanning, tanning and the finishing stages (Table 4.1)

The high electrical conductivity average value (14,640 μScm^{-2}) of the effluent indicates that the discharge of chemicals as cations and anions were higher in the wastewater. This was observed as shown before (table 4.3) having a variance value of p value 0.00 and F value of 90.29. The higher conductivity alters the chelating properties of water bodies. Therefore creating an imbalance of free metal availability for flora and fauna recorded that the electrical conductivity, pH, sulphides, BOD, and COD recorded in tannery effluent were much higher than the tolerance limits for industrial effluent discharged into land surface (Table 4.1). Similar studies in Hungary and Ireland revealed a high electrical conductivity of 16 260 μScm^{-2} (Song *et al*., 2004) which agrees with the ones obtained in this study (Table 4.1).

pH of the four different samples greatly varied (Table 4.3). Each section of the tannery plant had different pH values. Minimum pH was, however, recorded in chrome tanning section (pH 3.70) (Table 4.1) while liming section was having maximum pH (pH 11.0). Figure 4.2 is a bar graph which represents the differences in pH between the four main sampling points of the three sets of samples
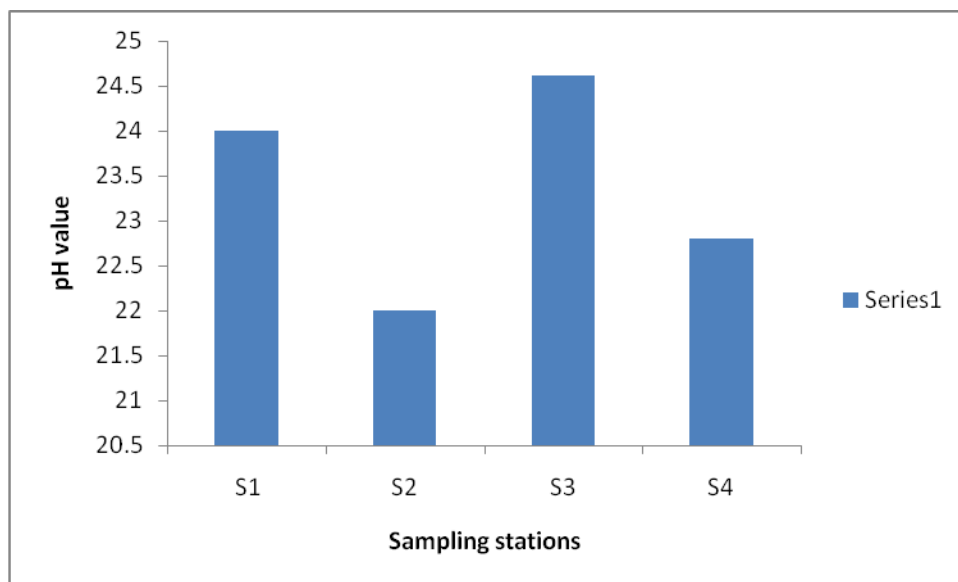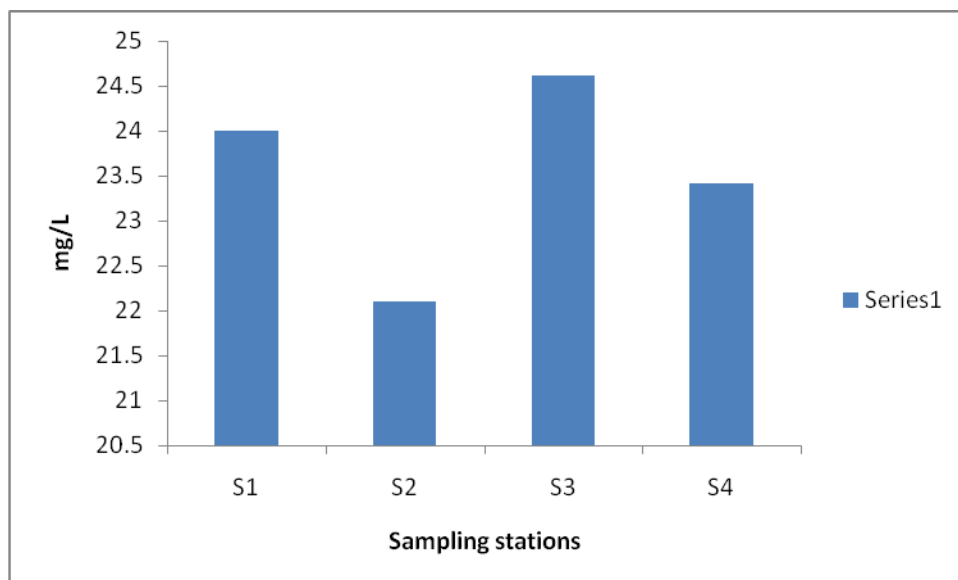

Figure 4. 3: pH variations in the four main sampling points of the three sets of samples

This variation in pH along the four sampling points could be attributed to different kinds of acidic or basic salts which are used in respective sections of leather tanning. The pH of the effluents from the pre-tanning/preparatory process was 11.0, which is highly alkaline. This and liming section/step utilize $CaCO_3$, Na_2S and NaHS which are basic in nature hence cause an increase in the pH of the effluent in this section. The pH of chrome tanning sections was in the range of 3.7, which is not surprising since it uses NaCl, H_2SO_4, formic acid and salts of Cr-III and Cr-VI.

At the final stage, the pH of the effluents was found to be 7.5 mainly because effluents from different sections (pre-tanning and the tanning stages) are mixed up thus the pH of the main effluent samples was found to be within the desirable limits (table 4.2). This pH value could also be attributed to the neutralization of the effluents which takes place in this stage. Similar studies done in Argentina revealed that the pH values of tannery effluent ranged between 4.5-7.5, while studies in tannery effluents in Kanpur showed pH variables ranging from 3.7-5.9. Other studies conducted in Nepal gave pH values ranging from 1-6 (Kaushik, 2003). This is within the range of results from Nakuru tanners, which could be due to lack of proper effluent treatment in the tanneries before disposal to the environment.

The heavy metals studied were found to vary in concentration with pH. A lower pH increases the competition between metal and hydrogen ions for binding sites. A decrease in pH may also dissolve metal-carbonate, and metal sulphate complexes, releasing free metal ions into the water column (Connell and Miller, 1984). This implies that as pH of the effluent increases the concentration of the various heavy metals increases and vice versa.

The temperature of the effluent is very important with regard to the chemical reactions, biological life and sludge treatment. The average effluent temperature did not, however, fall below 21°C. Thus, the tannery does not cause havoc as far as the environment is concerned.

Figure 4. 2: Temperature variations in the four main sampling points

From Figure 4.3 and Table 4.3, it is evident that the effluent temperatures significantly differed and were below the maximum permissible limits of 30 °C set by NEMA at point source (Table 4.2). High temperature raises the metabolic rate of surviving fish and microorganisms, leading to increased oxygen consumption and oxygen is less soluble at higher temperature. High temperature outside the optimum range for a prolonged period causes organisms to undergo stress and die (Song *et al.,* 2004). Sampling point 1 significantly differed from the rest since the temperatures were within the maximum permissible limit of 30 °C set by NEMA (Table 4.2).

Suspended solids include salt from raw skin / hide dusting; raw skin /hide trimmings; hair from the liming / dehairing process, which may contain lime and sulphides; and fleshing from raw skins /hides. Other solid wastes include wet-blue shavings, which contain chromium oxide (Cr_2O_3); wet-blue trimming, which is generated from finishing processes and contains chromium oxide, syntans and dye; and buffing dust, which also contains chromium oxide, syntans, and dye.
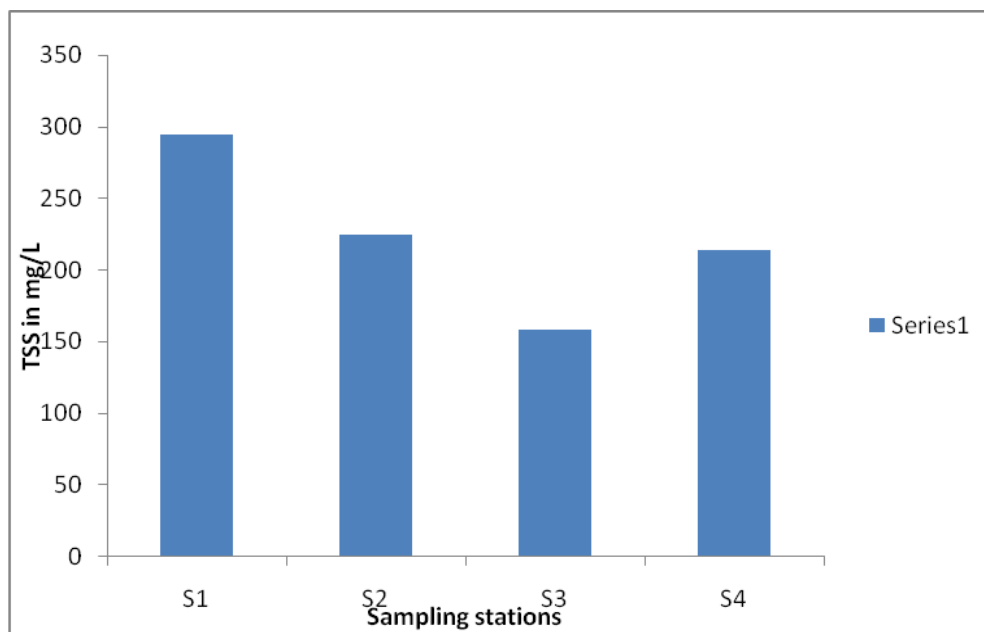
Figure 4. 3: Differences in TSS in four sampling points

Maximum limit of TSS allowed in liquid industrial effluents is 100 - 150 mg/L (Table 4.2). However, in this study most of the effluents examined were having the values greater than the permissible limits. Amount of total solids in pre-tanning section (S1) was 294.4 mg L^{-1} (Table 4.1) mainly due to the fact that in this section, protein, hairs, skin and emulsified fats are removed from the hides. Therefore these components result in the increased weight of total solids in this section.

The amount of total solids in tanning section (S2) was 224.60 mg L^{-1} (Table 4.1). This is mainly due to the extra suspended solids which result from the tanning and vegetable tanning especially the tannins which are difficult to break down. These cannot be removed easily and are intensively coloured, causing a non-toxic but highly non-degradable pollution load. The amount of total solids in final neutralization section (S3) was 158.25 mg L^{-1} which though lower, is still higher than the maximum permissible

limits. This could be attributed to the thorough sieving of the effluents which is practiced before the effluents are released into the sewage system. At the dumping site (S4), however, the value rose a bit to 214.30 mg/L and this upsurge could be attributed to the additional satiable solids already in the river where these effluents are dumped directly.

Total suspended solids have become a major problem in many countries (Song *et al.,* 2004). For example, countries such as South Africa`s (Cooman *et al.,* 2003) research results show TSS to be between 250-750 mg/L Italy (Khan and Aneyulub, 2005) has values varying between 200-800 mg/L while studies in India reveal that TSS values vary between 310 mg/L-900 mg/L (IUE 2001). These values concur with those recorded in Nakuru tannery that ranged between 158.25- 294.40 mg/L (Table 4.1) this could be due to lack of proper treatment of effluent before disposal.

Trivalent chromium salts (Cr III) are among the most commonly used tanning agents, accounting for the majority (approximately75 percent) of the Cr in the wastewater stream. The remainder is typically generated from post-tanning wet processes, stock drainage, and wringing. The reducing characteristics of tannery sludge serve to stabilize Cr (III) with respect to hexavalent Cr (Cr VI) content, as a result of the presence of organic matter and sulphide (Szpyrkowiez *et al*., 1991).

There was a variation of results in Nakuru Tanners for Cr (table 4.3) which seemed, however, higher compared to those from effluents of six different leather industries of Bara and Parsa districts (Nepal) whose amounts of this elements present in the effluents industries and water of Sirsiya River were found to vary between 0.12-345.00 mg/L. This could be due to the time of sampling and the type of treatment the effluent undergoes

which are poor and thus pose a hazard to the environment. Where the sampling was done immediately after the tanning process, has shown maximum concentration of chromium (Szpyrkowiez *et al.*, 1991).

Chromium and sulphide are among the most hazardous effluents of the tanneries (Song *et al.*, 2004). The use of excessive amount of these chemicals in tanning process gives rise to their high concentrations in the effluents. It has been reported that approximately one half of the sulphides used in tannery appear in the plant wastewaters. Chromium has been declared a carcinogen by the US EPA (FAO, 2001). The recommended limit for maximum amount of Cr in the tannery effluent is 1.0 mg L^{-1}. For Cr analysis, samples taken directly from the tanning section showed extremely high values of Cr (945 mg/L) (Table 4.1).

 The concentration of Cr in the sample of the pre-tanning section (S1) was (0.00 mg/L) (Table 4.1). This value could be attributed to the concentration of Cr in the pre-tanning section which is extremely low, far below detectable limits. Thus Cr concentration was not detected due to extremely low concentration or total absence. Studies from   Chile show Cr values of 148 mg/L (Kurt *et al.*, 2007) which are below the values reported in this study meaning this country tries to reduce the disposed of Cr unlike the Nakuru Tanners. While studies of the same in Egypt (Covington, 1997) show variations ranging from 600-1300 mg/L which is in the same range as values obtained from Nakuru Tannery of 680, 945 and 700 mg/L.

The sample taken from the effluent from the final/finishing section S4 showed Cr values of 700 mg/L (Table 4.1) which is much lower than the tanning sections S2 (945 mg/L)

but even then higher than the permissible concentrations. These high concentrations of chromium in all the tanneries could probably be due to the chromium salt (chromium sulphate salt) used for tanning.

At the dumping site (S4) right within the company before disposal to Gioto dumpsite, the level of Cr dropped a bit to 680 mg/L (Table 4.1). This could be attributed to complexation and coagulation of some of Cr by chelating agents in the river water leading to a slight decrease in the levels of detectable Cr (Stepniewska *et al*., 2004).

COD is the amount of oxygen required for the oxidation of organic matter present in the effluent samples. In this study, it was found that samples collected from the tanning site showed highest value for COD (9,107 mg/L). This could mainly be due to the fact that in vegetable tanning, different kinds of plant materials which produce tannins are used along with some other chemicals. Tannins are mixtures of different kinds of glucosides of various phenols. Their action is to combine with and between the collagen fibres of the skin. Use of this organic matter results in the increased COD (Kurt *et al*., 2007).
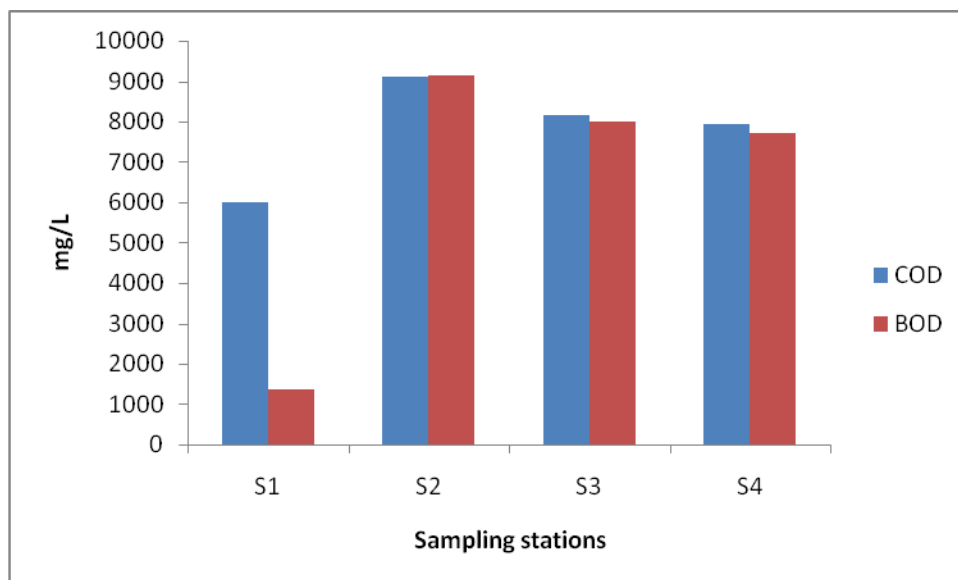
Figure 4. 4: COD and BOD variations in the four different sampling points in the three sets of samples.

The finishing section had (S4) low COD (8,145 mg/L) (Figure 4.5) possibly due to the use of neutral salts added up for the washing of the chrome from tanned hides. Effluents of this section had low concentration of chemically oxidizable materials and which justifies the low COD results.

The COD level of the sample from the pre-tanning (S1) section was, however, 6000 mg/L (Table 4.1). This could be because effluents of this section had low concentration of chemically oxidizable materials and is justified by the low COD results.

The permissible limits for COD set by NEMA is 250 mg L^{-1} (table 4.2). The COD values for all the samples were far above the recommended standards even at the dumping site (S4) where the COD values were found to be 7,930 mg/L. Similar results are observed by studies done in Chile (Guo *et al.,* 2006) on the evaluation of waste water quality based on chemical specific measurements and toxicity tests which demonstrated high values of

COD (2840-27, 600 mg/L), sulphate (230-35, 200 mg/L) and total solids (8600-87, 100 mg/L) (Cooman *et al*., 2003) and so continued discharge of the waste into the environment with these levels of COD values could lead to death.

BOD is the amount of oxygen required for the biodegradation of organic matter. It is almost directly proportional to the COD values but always less than COD. BOD is the parameter, which is widely used to determine the pollution load of wastewater.

The average BOD of tannery effluent was found to be 6555 mg /L (Figure 4.5), which was higher than that of the NEMA and WHO limits (100 - 300 mg/L). The BOD value of each sample was approximately equal to the COD value for the same reasons.

Sulphate levels in all the samples studied varied from 212.50 to 318.50 mg L^{-1}(Table 4.1). The high values for this pollutant could be attributed to the fact that sulphates are compounds of tannery effluent emanating from the use of sulphuric acid or products with high sodium sulphate content. These high concentrations of sulphate in all the samples could also be due to many auxiliary chemicals used containing sodium sulphate as a by-product of the manufacturer or chrome tanning powders containing high levels of sodium sulphate.
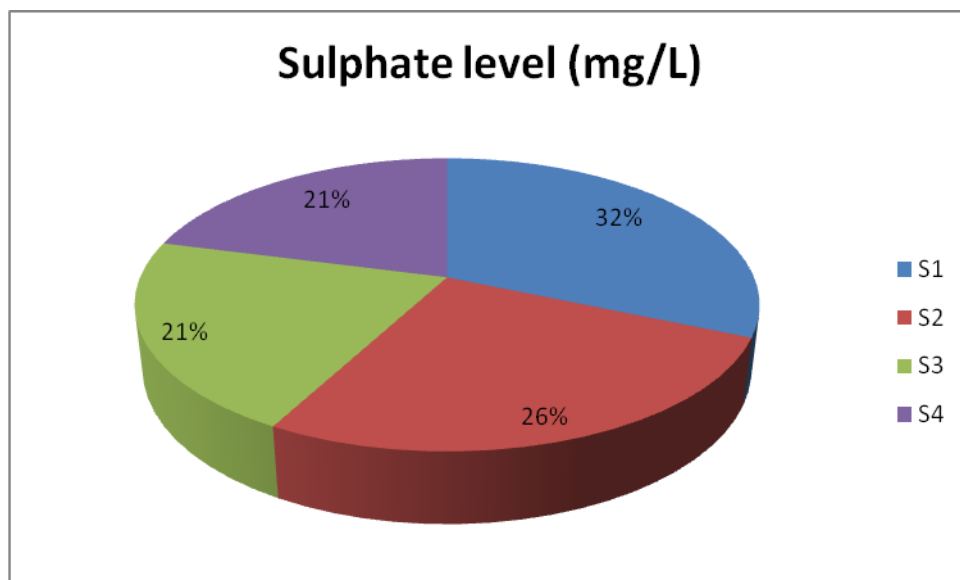
Figure 4.5: The percentage of sulphate content contributed by each sampling point to the total sulphates

Figure 4.7 shows that the nitrate levels in all the effluents studied varied between 39.40 to 83.30 mg L^{-1} within the four points sampled. These high levels of nitrate could be as a result of several components in tannery effluent containing nitrogen as part of the chemical structure and the nitrogen contained in proteinaceous material (from liming unhairy operation).
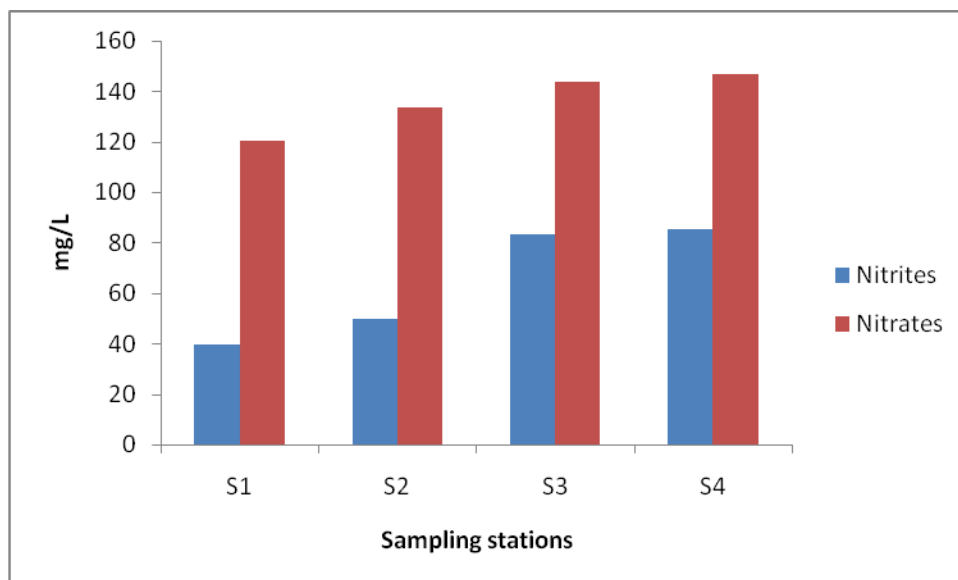
**Figure 4. 6: Variations in nitrates and nitrites in the four sampling points**

National and international bodies regulate the nitrate content in industrial effluent. NEMA set limit of 20 mg L^{-1} and the WHO limit of 6 mg L^{-1} nitrate levels are safe limits for babies. The samples from this effluent exceed these limits. Thus, nitrate concentration is considered to pose a problem for the domestic use of water from these rivers in which these effluents are deposited into.

The average nitrite level for all the four samples was 132.44 mg/L, a value lower than the mean concentration of nitrate but higher than the concentration limits stipulated by WHO and NEMA (Table 4.2). Bacteria quickly convert Nitrite (NO_2^-) to other more stable nitrogen ions and therefore, nitrate measurements typically represent the cumulative nitrate and nitrite concentrations (Szpyrkowicz *et al.*, 1991). The low nitrite level indicates that the tannery wastewaters had high bacteria levels meaning highly polluted with organic matter.

The average concentrations of Pb, P and Fe in the effluent were 5.13 mg/L, 10.88 mg/L and 4.25 mg/L, respectively. All these elements were present in higher concentrations

compared to the prescribed limits of WHO and NEMA. The tannery wastewater is contaminated with high levels of these pollutants. Irrigation using such contaminated water pollutes the soil, vegetables and crops, which when consumed cause serious health hazards. The presence of Pb and other heavy metals in the environment has become a major threat to plant, animal and human life due to their toxic effect and therefore must be removed from industrial effluent before discharge.
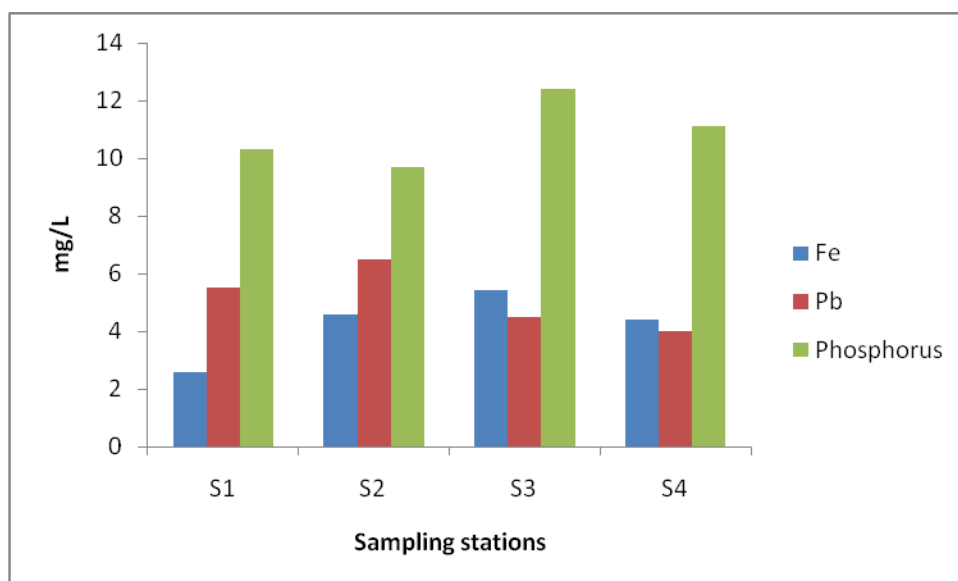

Figure 4. 7: Comparison of the concentration of P, Fe, and Pb in four samples

Hydrolysis of acidic material used in the tannery causes a decrease of water pH values. These acidic conditions cause the DO values to drop drastically in wastewater. Once deposited in rivers, the low DO level could result in the non-maintenance of conditions favourable to the gill-breathing aquatic organisms and increase the sensitivity of fish to chemicals.

There is an inverse linear correlation between TSS and DO levels and therefore, high TSS values always correspond to low DO level. In this study, the average DO level was 0.87 mg/L. Such occurrences could be possible due to the presence of high concentration

of TSS and turbidity from suspended solids that reduce water clarity; cloudy water absorbs more heat and blocks light penetrations. Therefore, increased turbidity increases water temperature and prevents photosynthesis which in turn reduces the concentration of DO since warm water holds less DO than cold water.
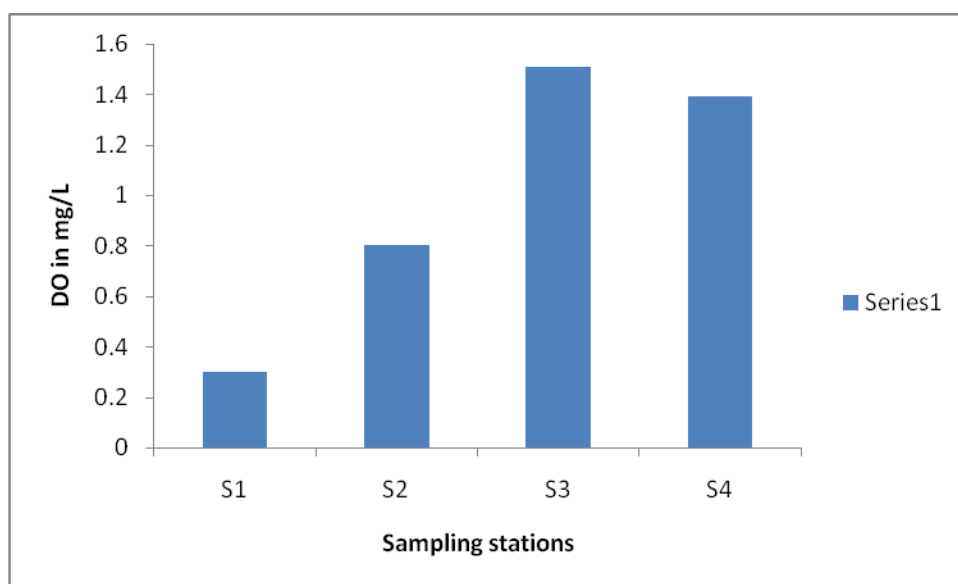
Figure 4. 8: Variations of the DO in the four sampling points of the three sets of samples

From figure 4.10 it is evident that there was a general increase in DO values from sampling points S1- S4 possibly due to treatment of the effluent by the tannery. This trend in the graph could be attributed to the biological degradation and complexation of the effluent over time (Mumford, 2010).

BOD and COD were found to vary with TSS (Figure 4.12) in the tannery wastewater samples. In this study, the average DO level was 0.87 mg/L. This could be the case due to the presence of high concentration of TSS and turbidity from suspended solids that reduce water clarity and cloudy water absorbs more heat and blocks light penetrations.
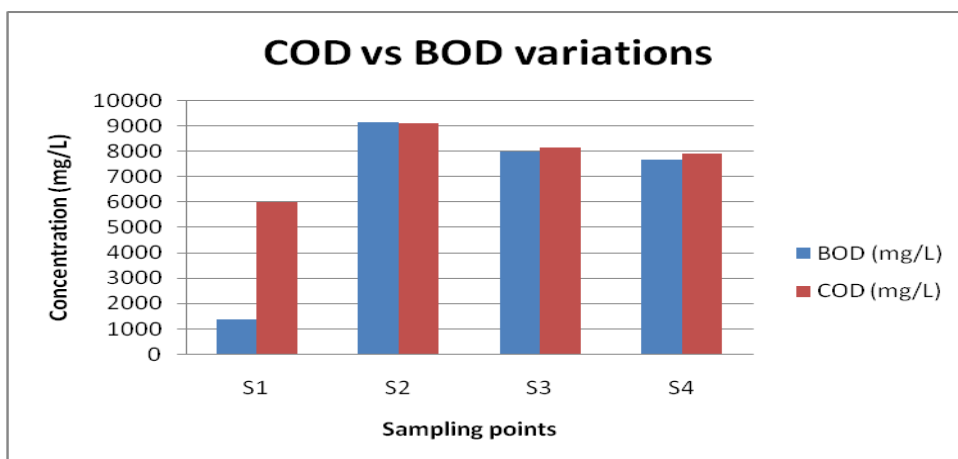
Figure 4. 9: Variation of BOD with respect to COD in the tannery wastewater samples

From this figures it is evident that all sampling points had almost equal values in BOD and COD with an exception of S1, this could be due to the chemicals in pertaining stage (S1) which is not properly treated.
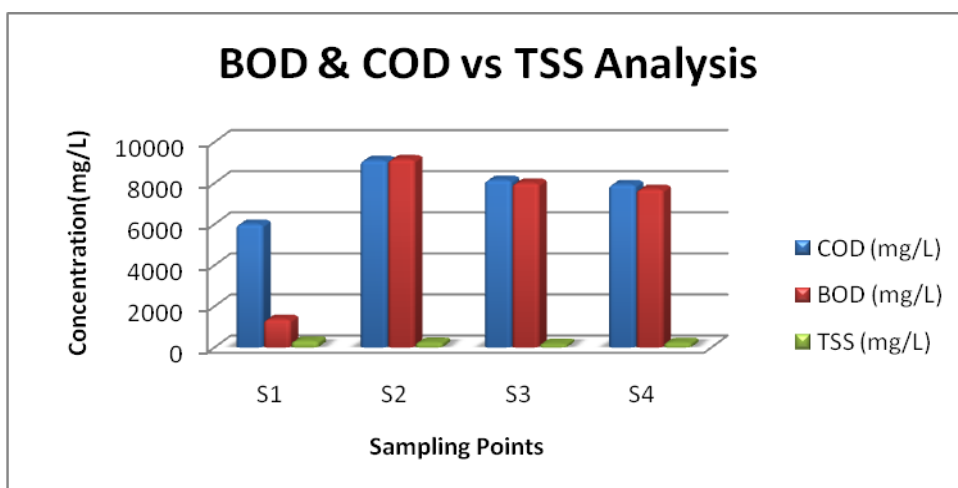
Figure 4. 10: Variation of BOD and COD with respect to TSS in the tannery wastewater samples

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The levels determined from samples prior to treatment clearly establish the fact that they are all well above the permissible limit as outlined by WHO and NEMA and no general trend was observed thus hazardous to the environment.

From the obtained results, it is clear that even though the NEMA and other international environmental regulators for the tanning industry are equally stringent, the pollution load coming from the tanneries is still heavy, and it is a problem both for the people living nearby, and for the river and ground water.

Most tanneries in the developing countries do not use conventional systems for treatment of the mixture of all production effluents. This is mainly because of the high cost of the treatment facilities thus no effective treatment is undertaken. Such a calamitous approach makes it impossible to meet environmental regulations.

The process modifications suggested by various groups have indicated that these values can be significantly brought down to decrease the pollution load on the treatment plant. To prevent pollution risks for waters and soils, proper effluent collecting and treatment systems must be established in the tannery fields as initial precaution.

5.2 Recommendations

Since the harmful effects of numerous chemicals generated by the leather industry are known, the following measures are recommended to be taken to alleviate the detrimental effects of tannery effluents.

5.2.1 Chemical Recovery and Reuse

Chemical recovery and reuse is an economically feasible alternative for the leather sector. With their short payback period, chemical recovery plants are financially attractive options. Leather industry should make all attempts to reduce its impact on the environment by making every effort to reuse and recycle chemical compounds.

5.2.2 Insitu removal of chromium and sulphide

Since Cr and S^{2-} are the two most important and harmful pollutants, they have to be removed from the effluents. This should be done as close as possible to the point where they are generated. Such liquids usually contain a quantity of chemicals: Cr (III) salts are potentially toxic - the risk of oxidation to chromate cannot always be excluded - and are valuable substances that should not be wasted. Thus, not only environmental but also economic considerations are important.

Cr and S^{2-} can be effectively removed from the effluents by bioleaching using potential bioleaching agents such as sulphur-oxidizing antioxidants. This is because removal using physical chemistry processes, such as coagulation/flocculation, adsorption and membrane separation do not solve the problem because of the transfer of contaminants from one phase to another.

The pollution load can also be decreased by introducing chrome tanning methods with high-exhaustion and fixing, methods based on direct recycle/reuse and recovery recycling techniques, screening of spent floats and washing waters.

5.2.3   COD and BOD Reduction

Approximately 75% of the organic load measured as BOD and COD is produced in the beam-house, with the main contribution coming from liming / dehairing processes. Dehairing is also the main generator of TSS. An additional source of COD / BOD is the degreasing process.

Measures to reduce the organic load of these tannery wastewaters include the following:

i.   Screening wastewater to remove large solids, this step removes all sorts of refuse that has arrived with the wastewater such as plastic, branches, rags, and metals. The screening process is used primarily to prevent the clogging and interference of the following wastewater treatment processes.

ii.   Use of an enzymatic dehairing process as an alternative to chemical dehairing order to recover hair for resale, reducing COD by up to 40–50 percent); enzyme based dehairing processes using proteases averts the use of lime and sulphide because of their environmental detrimental effects.

iii. If conventional lime dehairing process is used, filtering wastewater to recover hair before dissolution is highly recommended. This reduces COD by 15–20 percent and total nitrogen by 25–30 percent in mixed tannery effluent;

iv.   Recycling liming float reduces COD by 30–40%; nitrogen by up to 35%, sulphide use by up to 40%, and lime use by up to 50 percent;

v.   Use of easily degraded ethoxylated fatty alcohols, instead of ethoxylated alkyl phenols, as surfactants in degreasing;

vi.   Use of carbon dioxide (CO_2) deliming for light hides of less than 3 mm thickness. For thicker hides, the process requires an increase in the float temperature (up to 35 °C), and / or process duration, and / or the addition of small amounts of deliming auxiliaries.

5.2.4 TSS Reduction

Prevention and control measures for solid waste include the following:

i.   Reduction of inputs of process agents (particularly precipitation agents in wastewater treatment) to the extent practical.

ii.   Segregation of different waste / residue fractions in-order to facilitate recovery and re-use for example, to manufacture pet toys, pet food, leather fiberboard).

iii.   Recycling sludge as compost / soil conditioner or in anaerobic digestions for energy generation. Process sludge may be used for composting / agriculture after appropriate assessment for contaminants and potential impacts to soil and groundwater.

iv.   Disposing of non-recoverable and non-recyclable waste and sludge by appropriate methods, depending on the waste hazard classification.

5.2.5 Odours

Odours may result from raw hides and skins, putrefaction, and from substances including sulphides, mercaptans, and organic solvents. Prevention and control measures for odour emissions include the following:

i.   Prompt curing of raw hides

ii.   Reduction of the time that sludge remains in the thickener

iii. Dewatering thickened sludge by centrifugation or filtration process, and then drying the resulting filter cake

5.3 Challenges

Strict rules of the company on sampling, the company does not allow anyone to sample their waste water due to fear of reports by the publication of their effluents to the environment more so to the river Ndarugo and to the dumpsite in Gioto.

Sampling period was limited to three months and did not cover the recess period when the company does maintenance and repair. This was also hindered by the time given that the student was supposed to analyse the results and clear with the supervisor within a set period of time.

Lack of facilities to analyse more parameters and limited period of study, which is master's college to two years.

Distance of sampling was a major challenge especially when conducting the BOD analysis and temperature because this was always done either very early in the morning or very late in the evening to avoid confrontation by the management of the company.

5.4 Recommendations for further research

1. More research should be done on the tannery waste water disposal especially on other metals that were never covered in this thesis for instance elements like phosphorous, zinc, cadmium and nickel.

2. Work on greener methods of skin treatment apart from the aforesaid methodology to reduce pollution. This includes biological treatment using aerobic microorganisms and anaerobic treatment which converts the organic pollutants into a small amount of sludge and large amount of biogas.

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