

## Determination of Pollution Levels of Waste Water from Nakuru Tanners, Kenya

Nyabaro, Obed M.  
University of Eldoret  
msadamie@yahoo.com

Mosoti Douglas  
Kisii University  
douglasmosoti@yahoo.com

Muthoka, Titus M.  
University of Eldoret  
scientifictito@gmail.com

Onyancha Evans  
Kisii University  
eonyanacha@gmail.com

### 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 was undertaken. Water samples from four sampling points (S1 – Pre-tanning Stage, S2 – Tanning Stage, S3 – Post-tanning Stage 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,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  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  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  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  $\text{SO}_4^{2-}$  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  $\mu\text{g/L}$  and 6.50 mg/L. Sampling point S3 recorded the highest parameters of temperature, DO, Fe, P and electrical conductivity of values 24.62  $^{\circ}\text{C}$ , 1.15 mg/L, 5.40 mg/L, 12.40 mg/L and 14720  $\mu\text{SCm}^{-3}$  while S4 recorded the highest of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  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.

Keywords: Waste Water, Physicochemical Parameters, Pollution, Tanning

### Introduction

#### 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 come with 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; 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 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).

#### ***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 behavior and lack of 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).

#### ***General Objective***

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

#### ***Literature Review***

##### ***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 & Roether-Eduard, 1993). The 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).

##### ***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; 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; FAO, 2001).

##### ***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.

##### ***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).

The major pollutants in tannery wastewaters include: suspended solids, sulphates, sulphides, heavy metals, chlorides, organic matter, nitrates, nitrites, chrome and colorings.

## **Materials and Methods**

### **Study Area**

The study was done in Nakuru Tanners Co. Ltd. Located in Nakuru region of Kenya.

### **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 that is the effluents 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. After collection, the samples were transported to the chemistry laboratory of the University of Eldoret for refrigeration at 4 °C mainly to inhibit biological activity of samples.

### **BOD and DO Analysis**

Since samples for BOD analysis may change greatly during handling and storage, testing was done within 48 hours after collection. Chlorine being a strong oxidizing agent, 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 following the standard formula of APHA (1995).

### **COD Analysis**

In this case, the samples, standards, and blanks were heated at 150 °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.

### ***Determination of TSS***

The filters were washed using distilled H<sub>2</sub>O 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:

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### ***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.

### ***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.

### ***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.

### ***Determination of total phosphorus***

This was done using a UV-Vis spectrometer. 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.

### ***Determination of total Chromium (Cr)***

A 100 mL portion of each sample was taken, filtered through Whatman 42 filter paper and then acidified with concentrated HNO<sub>3</sub> to bring down the pH up to 2.0. A 100 mL of sample was taken and 5 mL concentrated HNO<sub>3</sub> 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.

### ***Determination of total sulphates***

This was done by acidifying a 10 mL portion of each sample with HCl and then BaSO<sub>4</sub> 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<sub>4</sub>. The amount of sulphate was then easily calculated using the equation:

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### ***Determination of Pb***

A 10 mL portion of each sample was taken, filtered through Whatman 42 filter paper and then acidified with concentrated HNO<sub>3</sub> to bring down the pH up to 2.0. A 5 mL of conc. HNO<sub>3</sub> 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.

### ***Determination of Fe***

10 mL portion of each sample was taken, filtered through Whatman 42 filter paper and then acidified with concentrated HNO<sub>3</sub> to bring down the pH up to 2.0. Approximately 5 mL of conc. HNO<sub>3</sub> 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. A 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.

## Results and Discussion

### Colour and Odour

The effluent released from Nakuru tannery industry was brown in colour and had an offensive odour. The colour of this effluent was 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 was due to the processing of skin and hides by soaking and liming. The yellowish brown colour hindered the penetration of sunlight causing depletion in the rate of oxidation process.

### Electrical Conductivity

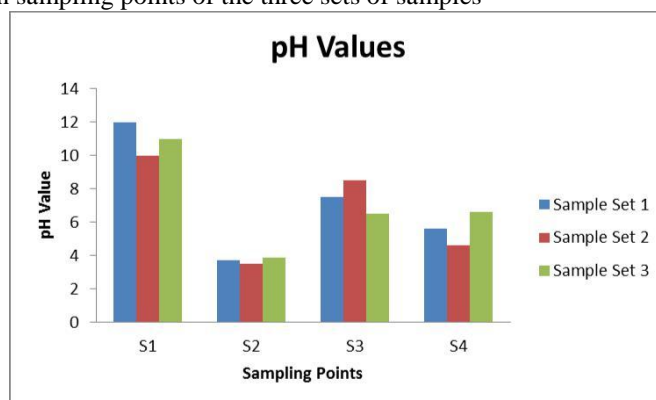
The high electrical conductivity average value ( $14,640 \mu\text{Scm}^{-2}$ ) (Table 1) of the effluent indicates that the discharge of chemicals as cations and anions were higher in the wastewater. The higher conductivity alters the chelating properties of water bodies. Therefore creating an imbalance 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 1. Averaged results obtained from the analysis of all the three set of samples from Nakuru tannery**

Sample	pH	Temp ( $^{\circ}\text{C}$ )	DO (mg/L)	COD (mg/L)	BOD (mg/L)	TSS (mg/L)	$\text{SO}_4^{2-}$ (mg/L)	Cr (mg/L)	Pb ( $\mu\text{g/L}$ )	Fe (mg/L)	$\text{NO}_3^-$ (mg/L)	$\text{NO}_2^-$ (mg/L)	P (mg/L)	EC ( $\mu\text{Scm}^{-2}$ )
S1	11	24	0.3	6,000	1,369	294.4	318.5	0	5.5	2.6	39.4	4	10.29	14550
S2	3.7	22.1	0.8	9,107	9,150	224.6	267	945	6.5	4.6	50	5	9.71	14670
S3	7.5	24.62	1.51	8,145	8,000	158.25	214.5	700	4.5	5.4	83.3	3	12.4	14720
S4	5.6	22.8	1.39	7,930	7,700	214.3	212.1	680	4	4.4	85.2	146.7	11.1	14620

### pH

pH of the four different samples greatly varied. Each section of the tannery plant had different pH values. Minimum pH was, however, recorded in chrome tanning section (pH 3.70) while liming section had a maximum pH (pH 11.0). Figure 1 is a bar graph which represents the differences in pH between the four main sampling points of the three sets of samples



**Figure 1. pH variations in the four main sampling points of the three sets of samples**

This variation in pH 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 (Table 1), which is highly alkaline. This and liming section/step utilize  $\text{CaCO}_3$ ,  $\text{Na}_2\text{S}$  and  $\text{NaHS}$  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  $\text{NaCl}$ ,  $\text{H}_2\text{SO}_4$ , 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. This pH value could also be attributed to the neutralization of the effluents which takes place in this stage.

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.

#### **Temperature**

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 did not cause havoc as far as the environment was concerned.

From Table 1, 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 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. Sampling point 1 significantly differs from the rest since the temperatures were within the maximum permissible limit of 30 °C set by NEMA (Table 2).

#### **Suspended Solids**

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<sub>2</sub>O<sub>3</sub>); 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.

#### **Total Suspended Solids (TSS)**

Maximum limit of TSS allowed in liquid industrial effluents is 100 - 150 mg/L (Table 4.5). However, in this study, most of the effluents examined had values greater than the permissible limits. The amount of total solids in pre-tanning section (S1) was 294.4 mg L<sup>-1</sup> (Table 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<sup>-1</sup> (Table 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<sup>-1</sup> (Table 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 to 214.30 mg/L and this upsurge could be attributed to the additional satiable solids already in the river where these effluents were dumped directly.

#### **Trivalent Chromium (Cr III)**

Trivalent chromium salts (Cr III) are among the most commonly used tanning agents, accounting for the majority (approx. 75%) 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 (Szpyrkowicz *et al.*, 1991).

There was a variation of results in Nakuru Tanners for Cr which was 680.00, 700.00, 945.00 and 0.00 mg/L (Table 1) 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 (Szpyrkowicz *et al.*, 1991).

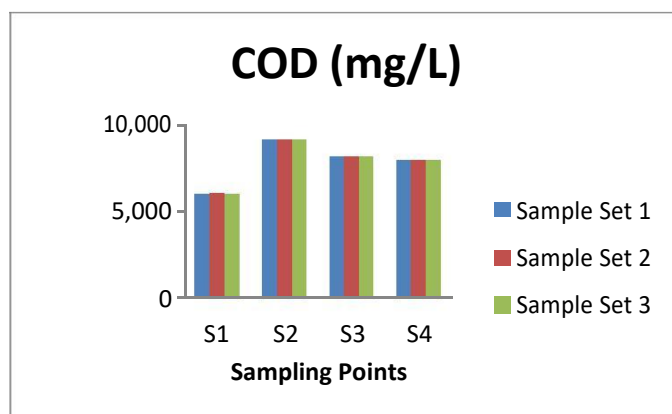
Chromium and Sulphide are among the most hazardous effluents of the tanneries (Song *et al.*, 2004). The use of excessive amount of these chemicals in tanning process gives rise to their high concentrations in the effluents. It has been reported that approximately one half of the sulphides used in tannery 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  $1.0 \text{ mg L}^{-1}$ . For Cr analysis, samples taken directly from the tanning section showed extremely high values of Cr (945 mg/L) (Table 1).

The concentration of Cr in the sample of the pre-tanning section (S1) was (0.00 mg/L) (Table 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. The sample taken from the effluent from the final/finishing section S4 showed Cr values of 700 mg/L (Table1) 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 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).

#### **Chemical Oxygen Demand (COD)**

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) (Table 1). 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 increase of COD (Kurt *et al.*, 2007).



**Figure 2. COD variations in the four different sampling points in the three sets of samples**

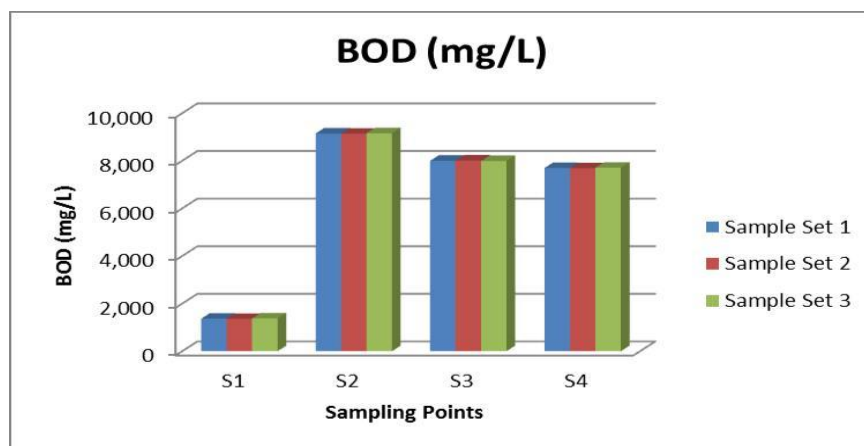
The finishing section had (S4) low COD (8,145 mg/L) (Figure 2) possibly due to the use of neutral salts added up for the washing of the chrome from tanned hides. Effluents of this section had low concentration of chemically oxidizable materials and which justifies the low COD results. The COD level of the sample from the pre-tanning (S1) section was, however, 6000 mg/L (Table 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 limit for COD set by NEMA is  $250 \text{ mg L}^{-1}$  (Table 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 (Table 2).

**Table 2. Maximum NEMA and WHO permissible values in waste water**

PARAMETER	WHO	NEMA
pH	5.5 – 8.5	5.5 – 9.0
Temperature (°C)	40	20 – 35
TSS (mg/L)	150	100
Electrical Conductivity ( $\mu\text{Scm}^{-2}$ )	400	400
Turbidity (NTU)	350	300
Pb (mg/L)	0.05	0.1
NO <sub>3</sub> <sup>-</sup> (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 <sub>2</sub> <sup>-</sup> (mg/L)	50	50
TDS (mg/L)	600	500
SO <sub>4</sub> <sup>2-</sup> and S <sup>2-</sup> (mg/L)	15	18
Cr mg/L	0.5	0.05
Phosphate (PO <sub>4</sub> ) mg/L	30	30

**Biochemical Oxygen Demand (BOD)**

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 4.6), 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.

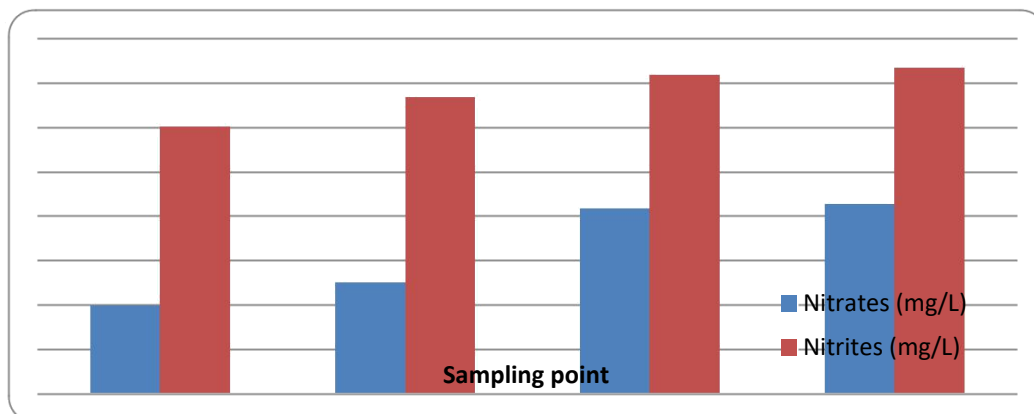


**Figure 3. Differences in BOD in four sampling points of the three sets of samples Sulphate Levels**

Sulphate levels in all the samples studied varied from 212.50 to 318.50 mg L<sup>-1</sup> (Table 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.

**Nitrates and Nitrites**

The nitrate levels in all the effluents studied varied between 39.40 to 83.30 mg L<sup>-1</sup> 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 unhairing operation).



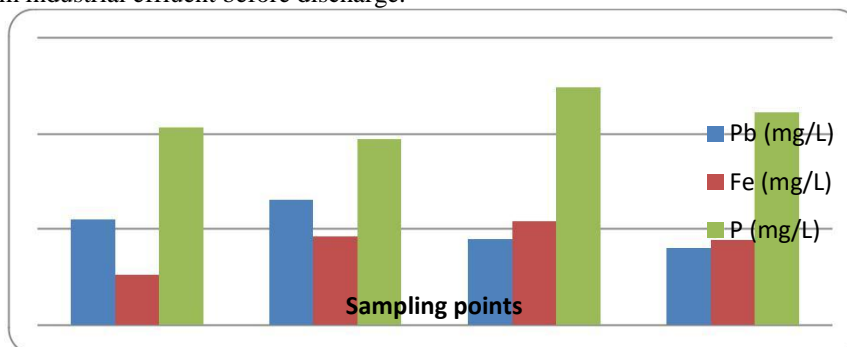
**Figure 4. Variations in nitrates and nitrites in the four sampling points**

National and international bodies regulate the nitrate content in industrial effluent. NEMA set limit of  $20 \text{ mg L}^{-1}$  and the WHO limit of  $6 \text{ mg L}^{-1}$  (Table 2) 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  $132.44 \text{ mg/L}$ , a value lower than the mean concentration of nitrate but higher than the concentration limits stipulated by WHO and NEMA (Table 2). Bacteria quickly convert Nitrite ( $\text{NO}_2^-$ ) 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.

#### **Lead (Pb), Phosphorus (P) and Iron (Fe)**

The average concentrations of Pb, P and Fe in the effluent were  $5.13 \text{ mg/L}$ ,  $10.88 \text{ mg/L}$  and  $4.25 \text{ mg/L}$ , respectively (Table 1). 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.

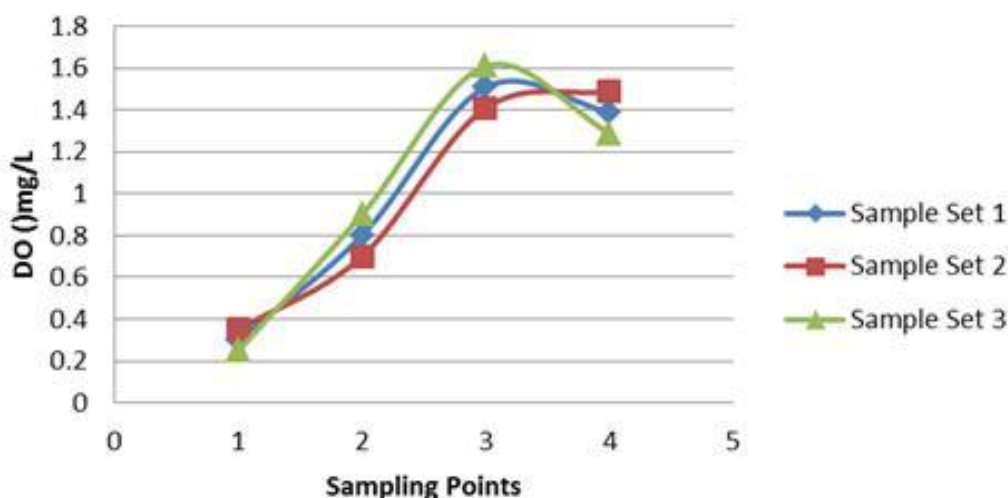


**Figure 5. Comparison of the concentration of P, Fe, and Pb in four samples Dissolved Oxygen (DO)**

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  $0.87 \text{ mg/L}$  (Figure 6). 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.

From Figure 6, 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).



**Figure 6. Variations of the DO in the four sampling points of the three sets of samples Conclusion**

The levels determined from samples prior to treatment clearly establish the fact that they are all 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.

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