Research Journal of Agriculture and Biological Sciences, 2(5): 209-217, 2006
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Characteristics of Tanning Industries in Nigeria for Aquatic Animals and Plants

[1]I.A. Oke, [3]J.A. Otun, [3]C.A. Okuofu and [2]N.O. Olarinoye

[1]Department of Civil Engineering, Obafemi Awolowo University, IleIfe, Nigeria.
[2]Department of Chemistry, Adeyemi College of Education, Ondo, Nigeria.
[3]Department of Water Resources and Environmental Engineering, Ahmadu Bello University, Zaria.

Abstract: The negative impact of industrial wastewaters on water bodies and environment cannot be over emphasised. The only way out of these negative impacts is proper protection of the environment through environmental pollution control measures. This paper provides an outline result of characterisation of tannery wastewaters. Wastewater samples were collected from twelve tannery industries in the northern part of Nigeria. The samples were subjected to laboratory tests (BOD, COD, pH, chloride, sulphate, TKN, some heavy metals and TP concentrations). The study revealed that tannery wastewaters is nutrient deficient, contain high chloride, some heavy metal, high COD, BOD, very high dissolved solids, COD: TKN and COD : TP ratio. The results show that tannery wastewater has mean concentration for BOD, COD, pH, dissolved solids, TKN, TP, chloride, sulphate, cadmium, chromium and zinc to be 1650.8 mg/l, 6590.2 mg/l, 9.6, 26436.2 mg/l, 20.8 mg/l, 26986.2 mg/l as NaCl, 1833.6 mg/l, 0.42 mg/l, 118.2 mg/l and 10.2 mg/l. The study revealed that 1.67 to 12.4% of the COD concentration would be degraded biologically. TKN: COD ratio revealed that tannery wastewater would require carbon source and TP: COD ratio (1:330) indicates that pre –chemical treatment before biological treatment of the wastewater would be required to reduce some of the pollutants especially chloride, dissolved solid and chromium.

Key words: Tannery industry, wastewaters, pollution control measures, heavy metals, COD:TP: TKN ratio, BOD

INTRODUCTION

Nigeria is one of the leather producers in West Africa. There are about forty tannery industries (process about 1860 tonnes of hides and skins per day) and three leather institutions in Nigeria. The wet process of tanning is concentrated at Kano which is on Latitude 12° 00‘ North and Longitude 8° 31‘ East and the largest city in the north of Nigeria as well as one of the most important commercial cities in the country[1]. Most of the tannery industries in Kano are located at challawa, sharada and bompai industrial estates and dry processes in the other centers (Fig. 1). The institutions are located in Zaria (NARICT and CHELTECH) and Kano (NARICT). Hides and skins are the major raw materials for tanning industries.

In the tanning process, animal hides and skins are treated to remove hair and non-structured proteins and fats, leaving an essentially pure collagen matrix. The hides are then preserved by impregnation with tanning agents. Leather production usually involves three distinct phases: preparation (in the beam-house); tanning (in the tanyard); and finishing, including dyeing and surface treatment. A wide range of processes and chemicals, including chrome salts, is used in the tanning and finishing processes. The tanning and finishing process generally consists of: soaking and washing (to remove salt, restore the moisture content of the hides and remove any foreign material such as dirt and manure), liming (to open up the collagen structure by removing interstitial material); fleshing (to remove excess tissue from the interior of the hide); de-hairing or de-wooling (to remove hair or wool by mechanical or chemical means); bating and pickling (to de-lime the skins and condition the hides

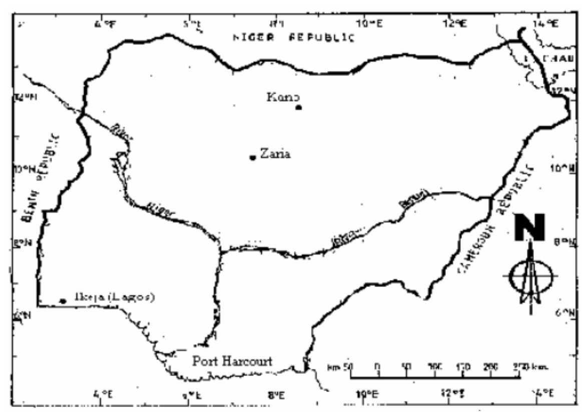

Fig. 1: Location of major Tannery Industries in Nigeria.

Corresponding Author: I.A. Oke, Department of Civil Engineering, Obafemi Awolowo University, Ile-Ife, Nigeria

to receive the tanning agents); tanning (to stabilize the hide material and impart basic properties to the hides); re-tanning, dyeing and fat-liquoring (to impart special properties to the leather, increase penetration of tanning solution, replenish oils in the hides and impart color to the leather); and finishing (to attain final product specifications). WGB[2] reports that there is a need for tannery industries to improveon environmental protection measure indicating that there is a need to put in place an effective wastewater treatment plant. In that line the main objective of this study is to characterize tannery wastewater with particular attention to physico- chemical to aid provision of an appropriate environmental protection facilities.

MATERIALS AND METHODS

Grabbed wastewater samples were collected according to standard methods (APHA[5]) weekly from twelve selected tannery industries in the Northern part of Nigeria (Fig.1) for a period of six months to characterize them. The characterisation was accomplished by laboratory testing of pH, Chemical oxygen demand (COD), BOD_5, heavy metals, sulphate, solids and phosphate concentrations. The BOD_5 and BOD_{21} concentrations were determined using respirometric method. Computations of BOD were carried out using expression:

$$BOD_t = \frac{(D_1 - D_2) - (B_1 - B_2)f}{p} \qquad (1)$$

For the determination COD closed reflux method was used. COD concentrations were calculated using expression:

$$COD = \frac{(A_1 - B_2) \text{x m x } 8000}{\text{ml of sample}} \qquad (2)$$

For phosphorus determination stannous chloride method was used. Phosphorus concentration was calculated using

$$P_s = \frac{M_a \text{ x } (1000)}{\text{ml of sample}} \qquad (3)$$

Organic–nitrogen concentration was determined using Macro-kjeldahl method while ammonia –nitrogen was determined using titrimetric method and computation was made using expression :

$$NH_3 - N(mg/L) = \frac{(A_a - B_b) \text{ x}280}{\text{ml of sample}} \qquad (4)$$

Measurement of sulphate concentration and all heavy metals were based on gravimetric method with drying of residue and AAS methods respectively as stated in APHA[3].

RESULTS AND DISCUSSIONS

The results were presented in three parts, namely: selection of sampling size, physical and chemical characteristics.

Selection of sampling size: It has been well documented that any study proposed to be carried out by sampling, the size of the sample affects the standard error[4,5]. Literature states that the adequacy for the acceptable precision of sample size can be stated in term of variance as:

$$V(\bar{x}) = \left(1 - \frac{n}{N}\right)\left(\frac{\delta^2}{n}\right) \qquad (5)$$

Loveday[6] describes standard deviation as a function of number of desired samples, probability of occurrence(p) and un-occurrence (q) of the sample as:

$$\delta = \sqrt{pq} \qquad (6)$$

With $p = 0.40$ (tannery industries from industries in Kano) and $q = 1 - p = 0.60$. N number of industries operating at the time of the study = 40 and assume a standard error to be 20%., expected sampling size can be computed as follows:

From:

$$V(\bar{x}) = \left(1 - \frac{n}{N}\right)\left(\frac{\delta^2}{n}\right) \qquad (5a)$$

$$0.20^2 = \left(1 - \frac{n}{40}\right)\left(\frac{0.40\text{x}0.60}{n}\right)$$

$$0.0400 = \left(1 - \frac{n}{40}\right)\left(\frac{0.240}{n}\right)$$

$$\frac{0.0400}{0.2400} = 0.1667 = \left(1 - \frac{n}{40}\right)\left(\frac{1}{n}\right)$$

and

$$0.1667 = \left(\frac{1}{n}\right) \quad ;n=5.2»5.0$$

Similarly, APHA[5] reports that because of variability from analytical and sampling procedures a single sample is insufficient to reach any reasonable desired level of confidence. It was suggested that if an overall standard deviation (the standard deviation of combined sampling methods and method of analysis) is known, the required number of samples for a particular confidence level in water and wastewater characteristics can be estimated as follows:

$$N = \left(\frac{ts}{U}\right)^2 \quad (6a)$$

Substituting for all the variables (s = 10.546, U = 10.0 mg/L and t = 2.02 at 95% confidence limit). Then number of samples required is 2.17[2] indicating 5. These results indicate that expected number of sampling size is 5 but 12 sampling sizes were selected indicating the 12 is adequate for maximum error of 20% statistical characterisation (upper limit characterisation).

Physical characterisation: The physical characterisation of wastewater involves temperature, colour, odour, turbidity, solids, density, flow rate and conductivity.

Temperature is basically important for its effects on other properties of wastewater. Average temperature of wastewater under investigation is 27.02°C. This result indicates that some reactions could be speeded up by the discharge of this wastewater in to the stream. It will also reduce solubility of oxygen and amplify odour due to anaerobic reaction (less dissolved oxygen).

Solid in wastewater could be grouped according to the relative size and condition of solids particles. Literature characterised solids in raw wastewater into four categories, based on the settling properties of the constituent material. The total solid material can be characterised into non-filterable and filterable solids fraction. The non-filterable fraction consists of settleable and non-settleable fraction and the filterable fraction consists of total dissolved solids (TDS) and colloidal fraction. Each of these fractions consists of volatile (organic) and fixed (inert) fraction. Evaluation of the suspended solid includes the settleable solid in the liquid streams and the total solid. Settled sludges are used to determine solids removal by any biological treatment system. Solids in wastewater may be present in suspension or in solution. They may be divided into organic matter and inorganic matter[7]. Total dissolved solid (TDS) are due to soluble materials whereas suspended solid (SS) are discrete particles, which can be measured by filtering the wastewater. Suspended solids (SS) concentration is the measure of amount of floating matter in the wastewater, because of its relationship with sedimentation tank, sludge formation and biological treatment suspended solids in the wastewater must be measured.

The suspended solids concentration was in the range of 5196.3mg/l to 10001.9 mg/l with a mean of 5564.6 mg/l (Table 1) with volatile suspended solids fraction of total solid varying from 0.048 to 0.138 and non-volatile fraction of total solid ranges from 0.861 to 0.942 (Table 2). Literature classified wastewaters with SS as follows: SS less than 100 mg/l as weak, SS greater than 100 mg/l but less than 220 mg/l as medium and SS greater than 220 mg/l as strong wastewater. Results of the study show that wastewaters from tannery industries can be classified as strong wastewater and cannot be discharged in to the stream, as it will encourage sludge formation the stream, which will in turn encourage anaerobic reaction that will affect self-purification of the stream. Similarly, dissolved solid concentration was in the range of 5604.3 to 55006.3 mg/l with the mean of 26436.2 mg/l with a fraction range of 0.519 to 0.846 of total solids (Table 1 and 2) indicating that tannery wastewaters contain soluble solid as well as floating solids which must

Table 1: Some physical properties of tannery wastewaters.

Parameter	Mean	Maximum	Minimum	FEPA[8] Limit
Temperature (°C)	27.02	28	26	< 41 °C
Suspended solid(mg/l)	5564.6	10001.9	5196.3	30
Dissolved solid (mg/l)	26436.2	55006.3	5604.3	2000
Total solid (mg/l)	32000.8	65008.2	10800.6	2030

Table 2: Fractions of some physical composition of tannery wastewaters.

Parameter	Mean	Maximum	Minimum	Standard deviation
Suspended solid fraction	0.174	0.154	0.481	0.084
Dissolved solid fraction	0.826	0.846	0.519	0.092
Non- Settle able fraction	0.878	0.914	0.869	0.056
Settle able fraction	0.122	0.134	0.086	0.014
Non- Volatile solid fraction of total solid	0.948	0.99	0.822	0.048
Volatile solid fraction of total solid	0.052	0.175	0.011	0.011
Non- Volatile solid fraction of suspended solid	0.899	0.942	0.861	0.047
Volatile solid fraction of suspended solid	0.101	0.138	0.048	0.015

be taken care of in wastewater treatment process design and sludge removal.

Chemical characteristics: In addition to physical characteristic, chemical characteristics tend to be more specific in nature than some physical parameters. Chemical properties are more useful in assessing the properties of wastewater samples. It includes oxygen demand, acidity and alkalinity, nitrogen, chloride, toxic metals, cyanides, phenols, oils and greases. Oxygen demand is important because organic compounds are generally unstable and may be oxidized biologically and chemically to a stable relatively inert end product.. An indication of organic oxygen demand content of wastewater can be obtained by measuring the amount of oxygen required for its stabilization either as BOD, COD or PV. Biological Oxygen demand (BOD) is the measure of the oxygen required by microorganisms whilst breaking down organic matter. Permanganate value (PV) is the amount of oxygen used by chemical (Potassium permanganate) to breakdown organicand inorganic matter while Chemical Oxygen Demand (COD) is the measure of amount of oxygen required by both potassium dichromate and concentrated sulphuric acid to breakdown both organic and inorganic matters. BOD and COD concentrations of the wastewater were measured, as the two were important in unit process design. The carbonaceous materials content of the wastewater can be estimated by the chemical oxygen demand. The typical chemical oxygen demand is subdivision into three main fractions, biodegradable (organic) chemical oxygen demand, non-biodegradable (inert) chemical oxygen demand and heterotrophic active biomass. The heterotrophic active biomass fraction is approximated as zero, as the influent is considered to be anaerobic, not seeded with recirculated-activated sludge or stabilization pond and the wastewater is not supporting active biomass generation. The non-biodegradable (inert) chemical oxygen demands are subdivided into particulate chemical oxygen demand and soluble chemical oxygen demand fractions, based on physical settling properties. The biodegradable (organic) chemical oxygen demand is subdivided into slowly chemical oxygen demand and readily biodegradable chemical oxygen demand fractions, based on bio-kinetic responses. The readily biodegradable chemical oxygen demand can be subdivided into short-chain volatile fatty acids (SCVFA) and non- short-chain volatile fatty acids (non-SCVFA or fermentable). These two divisions are normally represented by volatile fatty acids and fermentable readily biodegradable chemical oxygen demand. Alternatively, chemical oxygen demand is subdivision into two physical fractions, contains total soluble and total particulate chemical oxygen demand component. The non-biodegradable (inert) chemical oxygen demand fractions[7] can behave as conservative substances that can not be removed by the sedimentation process. The particulate material (particulate chemical oxygen demand) is mainly removed with the waste sludge and the soluble material (soluble chemical oxygen demand) passes through biological treatment processes unchanged. The biodegrad able (organic) chemical oxygen demand fractions are used by organisms in the biological process with the soluble material (readily biodegradable chemical oxygen demand) being used more rapidly than the slowly biodegradable chemical oxygen demand material, as measured by oxygen or nitrate utilization rate tests. The short-chain volatile fatty acids fraction is increased in a wastewater with the solubilisation of slow biodegradable chemical oxygen demand to readily biodegradable chemical oxygen demand and the fermentation of fermentable readily biodegradable chemical oxygen demand to short-chain volatile fatty acids[7,16]. The wastewater under investigation has an average COD concentration of 6590.2 mg/l of which non-biodegradable fraction has the range of 0.876 to 0.986 fractions (Table 3). Biodegradable fraction of COD (slowly and readily) has the range of 0.014 (slow 0.008 against 0.006 for readily) to 0.144 (0.047 for slow and 0.097 for readily). This indicates that about 1.4 to 14.4% of the influent COD will be degraded biologically. BOD_5 concentration of the wastewater has a maximum value of 1860 mg/l, a minimum of 800 mg/l, an average of 1650.8 mg/l. BOD_{21} concentration has a mean of 5200.0 mg/l. High COD and BOD_5 concentration observed in the wastewater might be due to the use of chemicals, which are inorganic that are oxygen demand in nature or variation in the process or method of production. Results of BOD_5 and COD fall in the range documented in previous studies elsewhere (Tables 4 and 5).

pH has been well defined in literature as negative logarithms of hydrogen ion concentrations. Low pH has a more effective bactericidal, virucidal and crysticidal action in disinfections provided by chlorination. The role of pH in wastewater is also associated with corrosivity, alkalinity, hardness, acidity, chlorination, coagulation and carbon dioxide stability. pH of wastewater is the intensity of acidity or alkalinity of the wastewater, which is actually the measure of hydrogen ion concentration in the wastewater. pH value of wastewater has no health implication but many chemical reactions are controlled by the pH value. Biological activities and some chemical treatment processes are usually restricted by pH. Wastewater for biological process is fairly narrowed in the pH range of 6-8 as highly acidic or highly alkaline wastewaters are undesirable because of corrosion hazard to sewers and possible difficulties in the treatment. pH of the wastewater ranges from 8.3 to 10.50 with a mean of 9.6. FEPA[8] recommends pH value of range 6.0 – 9.0 for effluent to be discharged into stream, with this range of 8.3 to 10.50 for tannery wastewaters, the wastewaters are

Table 3: Some chemical properties of tannery wastewaters.

Parameter	Mean	Maximum	Minimum
pH	9.6	10.5	8.3
Biochemical oxygen demand (mg/l)	1650.8	1860	800
Chemical oxygen demand (mg/l)	6590.2	15000.9	4800
Chloride (as NaCl, mg/l)	26986.2	39980.4	18290
Chromium (mg/l)	118.2	180.8	85.7
Cadmium (mg/l)	0.42	1.26	0.08
Zinc (mg/l)	10.2	15..8	8.6
Sulphate (as SO_4 mg/l)	1833.6	3475.1	748.2
Total phosphorous (as P, mg/l)	20.8	35.6	14.6
Nickel (mg/l)	0.32	1.46	0.18
Total Kjeldahl nitrogen (TKN, mg/l)	2045.8	3108.2	448.2
Oil and grease (mg/l)	1500.6	3350.8	1168.6
Sulphide (S^{-2}, mg/l)	204.2	295.1	180.5

Table 4: Characteristics of raw tannery waste water

Parameter (mg/l)	Raw waste water	Homogenisation	Primary clarifer
Total COD	5094	4506	2216
Soluble COD	2336	1345	1187
BOD_5	1760	1402	958
SS	2229	2988	794
VSS	-	-	506
TKN	358	367	226
Org N	223	209	62
NH_3-N	135	158	164
Total P	-	-	5.1
Total Cr(Cr^{+3})	116	132	41
Sulpher ($S^{=}$)	51	47	27

Table 5: Characteristics of tannery wastewaters from literature.

	Source (WBG[2])	Source (Nemerow[15])	
Parameters	Range	A	B
BOD (mg/l)	900-6000	6687	58340
Chromium (mg/l)	200-800		
Sulphide (mg/l)	200-1000	28900	20000
TKN (mg/l)	800-4000		
COD(mg/l)	2400-14000		
Separated Process			
(Cl^{-}, mg/l)	200-70000		
Combined Process			
(Cl^{-}, mg/l)	5600-27000	114760	272885
Hardness (mg/l)		61570	42200
Total Solid (mg/l)		340800	485930
Volatile Solid (mg/l)		66000	70420

alkaline, can not be discharged into stream based on FEPA[8] limit because it will be harmful to man, aquatic animals and will disturb biological activity (self purification) of the stream if discharged untreated.

Tannery wastewater studied contains 3108.2 mg/l of TKN (as maximum) and 448.2 mg/l as minimum with 2045.8 mg/l as the mean. The presence of TKN can be attributed to the use of animal's hides and skins in the production line of tannery materials.. Nitrogenous compounds, termed total nitrogen, are in the form of organic (proteinaceous) nitrogen and inorganic total ammonia (NH_3 –N plus NH_4 –N) and oxidized nitrogen compounds, such as nitrate (NO_3-N) and nitrite (NO_2 -N) represented togetherby the total Kjeldahl nitrogen (TKN). The oxidised nitrogen compounds are usually present in low quantities in typical wastewaters. The inorganic total ammonia nitrogen exists in solution as ammonia (NH_3 -N) and ammonium (NH_4 -N). These fractions depend on the pH, with NH_4 -N being predominant at conditions with a pH below 7, as found in the wastewater sludge. It is difficult to fractionate organically bound nitrogen (e.g. protein, urea) into biodegradable and non-biodegradable soluble and particulate fractions of nitrogenous compounds. Bacterial decomposition and hydrolysis convert organically bound nitrogen to ammonia and ammonium. The non-biodegradable particulate and soluble nitrogen fractions are handled in a similar fashion as the conservative non-biodegradable (inert) chemical oxygen demand. The evaluation of the total Kjeldahl nitrogen and the NH_3 – N plus NH_4 –N fractions in wastewater is used to determine the changes in total Kjeldahl nitrogen to chemical oxygen demand nutrient ratio and the concurrent ammonia fraction changes across the treatment plant. This result of TKN seems higher than expected for value for wastewater to be treated biologically, but there is away of inducing TKN in nitrogen deficient wastewaters (either by adding chemical nutrient to support biological treatment or seeded with sludge to improve oxidation). This result of the TKN is similar to the result of classification of tannery wastewaters elsewhere (Tables 4 and 5).

Like nitrogenous compounds phosphorus compounds are also found in wastewaters, predominantly as phosphates and can be categorized by physical means (dissolved and particulate fractions) and by chemical means as phosphate compounds. The chemical fractions consist of dissolved inorganic orthophosphate (o-PO_4), polyphosphate or condensed phosphate and organically bound phosphate. The orthophosphates (PO_4^{-3}; HPO_4^{-2}, H_2PO^{4-} and H_3PO_4), usually the predominant fraction in wastewater, are available for biological metabolism without further breakdown. The polyphosphates include two or more P atoms ($P_3O_{10}^{-5}$, $P_2O_7^{-2}$) in a complex molecule and revert together with the organic phosphates through a slow-rate hydrolysis process to the soluble dissolved inorganic orthophosphate forms. The organic phosphorus fraction refers to phosphate in organic chemicals (cells, pesticides and detergents) for which typical soluble and particulate constituent percentages are not available. Evaluation of biological treatment plant is based on the total phosphorous and inorganic orthophosphate fractions of liquid and sludge streams to determine the changes in the total phosphorous to chemical oxygen demand ratio and the concurrent inorganic orthophosphate fraction change across the biological treatment plant[7]. The wastewater under investigation has total phosphorus of a maximum value of 35.60 mg/l, minimum value of 14.6 mg/l and a mean of 20.80 mg/l of TP as phosphorus. The presence of this pollutant can be attributed to washing activities(through the use of detergent and other phosphate products). This concentration of TP seems to be low to support biological treatment of tannery wastewater, but the way out is to increase TP source through seeding and chemical nutrient addition.

Chlorides in wastewater indicate the contact with human excreta (urine, or with common salt). Effect of chloride on biological treatment process has been discussed in standard environmental literature. Chloride concentration was in the range of 18290 to 39980.4 mg/l as NaCl with the mean of 26986.2 mg/l as NaCl indicating that tannery wastewaters under investigation was in contact with chloride source, FEPA[8] limits for chloride in wastewater is 600 mg/l with lower concentration of chloride in tannery wastewater it will be harmful to man, aquatic animals and biological treatment process.

It is well known that day-to-day wastewater constituent concentrations usually exhibit considerable variations, but the ratios of constituents accommodate such fluctuations to some extent, the constituent ratios can be used as fairly representative benchmarks to characterise the wastewater for biological treatment evaluations. Wastewater with high nutrient ratios will not produce adequate denitrification for certain biological process configurations, which is a prerequisite for tertiary treatment. The strength of the settled sewage must also be considered, together with the total Kjeldahl nitrogen to chemical oxygen demand ratio, as the chemical oxygen demand content in the settled sewage contributes to the establishment of anaerobic conditions in the anaerobic zone of the biological treatment reactor. Substantial chemical oxygen demand consumption takes place during the biological process and about 8.6 mg/l chemical oxygen demand is needed to reduce 1 mg/l nitrate nitrogen to nitrogen gas during denitrification and about 50 mg/l chemical oxygen demand, is required per 1 mg/l total phosphorous removed. The most efficient type of chemical oxygen demand fraction utilised during denitrification and phosphate removal is volatile fatty acid, which can be increased in the sedimentation process. A low strength biological process feed (chemical oxygen demand less than 250 mg/l[7]) can therefore reduce the biological process performance. At a total phosphorus to total chemical oxygen demand ratio of greater than 0.02 chemical treatment will be necessary to precipitate phosphorus. When the total Kjeldahl nitrogen to chemical oxygen demand ratio is higher than 0.11 and the volatile fatty acid content is low (volatile fatty acid less than 50 mg/l), an external carbon source should be used, the anaerobic zone of biological reactor must be enlarged or sedimentation must be implemented. Sedimentation is currently incorporated as a standard practice worldwide at many biological treatment processes, even for industrial wastewater treatment plant with feed total Kjeldahl nitrogen to chemical oxygen demand ratios of lower than 0.11[7]. With TP to COD ratio of the wastewater been 0.0030 less than 0.02 chemical treatment would not be needed. Also with TKN to COD ratio been 0.31, which is greater than 0.11 carbon source will be required. BOD: TKN: P ratios are important in process design. Horan[9] highlights that BOD: TKN: P greater than 100; 5;1 is for anaerobic system and less than the value is for aerobic. The maximum COD: TKN: P ratio of the wastewater is 421:87: 1, mean ratio of 326:101:1 and minimum ratio of 324: 33: 1 with BOD :TKN: P ratio as 421 :87:1 for maximum; 52:87:1 for mean and 79:98:1 minimum. These are clear indication that carbon and phosphorus are available but in deficit quantity while nitrogen content is more than enough for effective biological treatment process. Therefore biological treatment of tannery wastewater is possible but efficiency can be improved upon if nitrogen source can be reduced, carbon and phosphorus can be added or if sedimentation tanks can be provided for nitrogen content to be reduced.

Other pollutants of a greater importance in industrial wastewaters include heavy metals (which are zinc, aluminium, lead, manganese, iron, chromium, copper and cadmium), sulphide and sulphate, oil and grease. The accumulation of metals in an aquatic environment has direct consequences to man and to the ecosystem. Interest in metals like zinc which is required for metabolic activity in organisms, lies in the narrow "window" between their essentiality and toxicity. Others like cadmium and lead exhibit extreme toxicity even at trace levels. Zinc is present in wastewater streams from steelworks, rayon yarn, fiber manufacture, ground wood-pulp production and recirculating cooling water systems employing cathodic treatment the plating and metal –processing industry. Nickel originates from the metal processing industries, steel foundries, motor vehicles and aircraft industries, printing and in some cases the chemical and food processing industry. Zinc, lead and cadmium are common pollutants, which are widely distributed, in the aquatic environment. Their sources are mainly from weathering of minerals and soils; atmospheric deposition; industrial effluents, domestic effluents, urban storm water runoff and spoil heaps[7]. Extensive literature on the aquatic toxicity of zinc and especially its toxicity to fishes has been reviewed by many authors. Zinc is unusual in that it has low toxicity to man, but relatively high toxicity to fish. Lead is present in wastewater mainly from storage –battery manufacturing, petroleum refinery and run-off. Lead is defined by the United States Environmental Protection Agency (USEPA) as potentially hazardous to most forms of life and is considered toxic and relatively accessible to aquatic organisms. Low lead concentrations affect fish by causing the formation of coagulated mucous over the gills and subsequently over the entire body and thus cause the death of fish due to suffocation. Lead is bio-accumulated by benthic bacteria, freshwater plants, invertebrates and fish. The chronic effect of lead on man includes neurological disorders, especially in the foetus and in children. This can lead to behavioural changes and impaired performance in IQ tests[11,12]. Cadmium is from metallurgical alloying, ceramics, electroplating, photography, pigment works, tannery printing, chemical industries and lead mine drainage. Cadmium has been found to be toxic to fish and other aquatic organisms[7]. The effect of cadmium toxicity in man includes kidney damage and pains in bones (Itai-itai disease). Cadmium also has mutagenic, carcinogenic and teratogenic effects. These heavy metal concentrations were determined because of their importance as nutrient and as toxic substance at a certain concentration. Hexavalent chromium is present in the effluents produced during the electroplating, leather tanning, cement, mining, dyeing and fertilizer and photography industries and causes severe environmental and public health problems. Hexavalent chromium has been reported to be toxic to animals and humans and it is known to be carcinogenic[10]. Its concentrations in industrial wastewaters range from 0.5 to 270.000 mg·/L. The tolerance limit for Cr(VI) for discharge into inland surface waters is 0.1 mg/l and in potable water is 0.05 mg·/L. Chromium and its compounds are widely used in plating, leather tanning, cement, shell, dye and photography industries, producing large quantities of toxic pollutants which cause severe environmental and public health problems. Among the most interesting waste treatment problems is that posed by hexavalent chromium which is on the list of priority pollutants defined by the FMENV and other similar authorities. It is well known that cobalt, chromium and nickel are among the most toxic of elements, it is necessary to develop methods to lower their presence in contaminated media to innocuous quantities. Heavy metal concentrations in tannery wastewaters are not well documented but statistical information on these heavy metals is as shown in Table 3. The results indicate that these heavy metals are not in high concentrations like chloride but their removal is essential to prevent accumulation in aquatic animals and in order to comply with specified limits by FMENV and other relevant authorities guidelines.

Sulphate rich effluents can be treated biologically when sulphates reducing bacterial (SRB) and organic matter are present. The products of the biological sulphate removal technology are sulphide and alkalinity, which contribute to the pH increase of the treated wastewater. It has been reported that sulphides are fatally toxic to humans at gaseous concentration of 800 to 1000mg/l[11]. Sulphate concentration of the wastewater under investigation is greater than 800 mg/l which indicates that

Table 6: Treatment options[13]

	District I		District II		District III	
Parameters mg^{-1}	Initial[1]	Treated	Initial[2]	Treated	Initial[2]	Treated
Total COD	5756	1050	4705	1108	4180	1120
Soluble COD	1170	-	1600	-	1495	-
SS	2640	248	2300	128	2070	205
TKN	363	208	- -	250	175	
Total Cr (CR^{+2})	42	<0.5	167	1.9	65	035
Sulphur (S^{-1})	78	24	42	10.6	68	16

Table 7: Water quality for aquatic animals and plants[14]

	Freshwater fisheries		Water to be used for	
Parameters	Salmonids	Coarse fish	Irrigation of crops	Watering of livestock
BOD_5 (mg/L)	3.0	6.0		
Total Ammonia as				
Nitrogen (mg/L)	0.031	0.16		
Suspended solid (mg/L)	25	25		
pH	6-9	6-9		
Cadmium (mg/L)	5	5	5	5
Zinc (mg/L)	10-125	7-500	1000	2500
Phosphate	20.6	20.6		
Surfactants as lauryl sulphate	4.12	4.12		

the wastewater could cause serious damage to human and can not cause corrosion in sewerage system. Result of sulphide, oil and grease in the wastewater under investigation is as shown in Table 3. This indicates that proper treatments are required for removal of these two pollutants that are known as inhibitors in biological treatment processes.

Comparison with data from literature: Orhon *et al*.,[13] states that tannery effluents exhibit all the characteristics of a strong wastewater, mainly with respect to their organic carbon and nitrogen content. The study conducted on wastewaters from an organized industrial district housing a large number of tanneries, the concentrations of conventional polluting parameters such as COD and TKN were assessed as 5 000 and 350 mg/l respectively. It was reported a COD/N ratio was around 14 as outlined in Table 4. The result is slightly different from the current result which might be attributed to the following reasons: tanneries in kano process raw hides and skins which are bound to contain higher pollutants, tanneries studied by Orhon *et al*.,[13] involves in processing processed hides and skins; composition of raw material and chemical for processing varied; and Variation in recommended processes by regulatory authorities influence expected pollutants.

Artiga *et al*.,[14] describes tannery wastewaters as wastewaters with salt (chloride ion), fat, protein, ammonia, sulphides, chromium and polyphenolic compounds. Table 5 shows result from Nemerow[14], which shows that pollutants varies with processes and methods. Suggested treatment processes were highlighted in Orhon *et al*.,[13] as plain settled wastewater was observed to lower the COD concentration to 2 200 mg/l, the corresponding TKN level obtained was 225 mg/l (corresponding to a reduction of only 37%). Chemical treatment provided a slight improvement in TKN removal as outlined in Table 6. The limitations of the physico-chemical treatment could be explained by the fact that TKN in tannery wastewaters involved a significant NH_3-N fraction remaining intact, if not slightly increased due to ammonification during settling. Aerobic biological treatment has been prescribed for simultaneous carbon and nitrogen removal from tannery wastewaters in literature[13].

Comparison with water quality for aquatic animals and plants: In order to justify the quality of the industrial wastewater for aquatic animals and plants the results were compared with standard documented in literature such as Ellis (1981) and it was found that the quality of the wastewater is suitable for neither aquatic animals nor plants. Therefore there is a need to save the environment from pollution and collapse of food chain. Table 7 contains standards as stated in Ellis[16].

Conclusions: It can be concluded that:
tannery wastewaters requires a bacterial seeded acclimated to the wastewaters because of the alkalinity nature of the effluents.

There is a need to decrease nitrogenous compounds, dissolved solids and chromium concentrations to aid biological treatment of the wastewater.

ACKNOWLEDGEMENT

The authors wish to acknowledge Ahmadu Bello University, Zaria Nigeria through the Department of Water Resources and Environmental Engineering for providing some valuable equipment. Also we wish to acknowledge Mr. P.C Alika, Late Halilu Buhari, Yahaya Yakubu, Dahiru, N, Garba, S.S; Oladoja, B.I; Adalemo, A; Ariyo,S.K; Aneke, I.C and Ajayi, T.O all of Department of Water Resources and Environmental Engineering for their role in the research work.

Abbreviation and symbols:

BOD: Biochemical Oxygen Demand
COD: Chemical Oxygen Demand
DO Dissolved Oxygen
mg/l milligrams per litre
SS: Suspended solids
D_1 and D_2: initial and final dissolved oxygen of the sample respectively
(mg/l)f ratio of seed in the sample to seed in the controlp decimal volumetric fraction of sample used.
B_1 and B_2: initial and final dissolved oxygen of the seeded control respectively
(mg/l)A_1: ml of FAS used for the blank
B_2: ml of FAS used for the sample
M: Molarity of FAS
FAS: Ferrous ammonium sulphate
M_a: equivalentphosphorus from calibrated plot.
A_a: volume H_2SO_4 used for the sample
B_a: volume H_2SO_4 used for the blank
NARICT: National Research Institute for Chemical Technology
CHELTECH Chemical and Leather Technology
N: Number of sample sizet tudent
t: statistic for a given confidence level.
s: overall standard deviation = products of all deviations.
U: acceptable level of uncertainity (±10 mg/l).

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