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Assessment of Tannery Industrial Effluents from Kano Metropolis, Kano State, Nigeria

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Abstract: The aim and objective of the study was to determined pollutant levels in tannery industrial effluent from kano metropolis, Nigeria. Effluents from five tannery industries were characterized and the major sources of industrial pollution determined. Levels of heavy metals (Cu, Zn, Co, Mn, Fe, Pb and Cr) were determined using Atomic absorption Spectrophotometric method, while pH, Eh, DO, TDS, Temperature, sulphate, nitrate and phosphate were also determined using standard procedure. The results of the study showed that effluent quality discharged between tanneries differed significantly. Effluent chromium concentrations varied between 1.02±0.13 to 1.56±0.06 mg L^{-1}, which are above WHO and FEPA limit of 1.0 mg L^{-1}. Hafawa Enterprise Tannery, Unique Leather Finishing had significantly high lead concentrations, while Great Northern Tannery could be a potential source of Iron contamination in this area. Mean levels of Zn for Tannorth Tannery Limited were above maximum permissible limits set by FEPA and WHO. Mean levels of sulphate, nitrate and dissolved Oxygen were also above maximum permissible limits for the entire tanneries studied. Mean values of pH total dissolved solid, phosphate, temperature, Cu, Co, Mn and Redox potential generally were below maximum and minimum permissible limits for effluent discharged into rivers. The monthly variations in the entire tannery fell within the range set up by FEPA and WHO for the discharged of tannery effluent into river. The study serves to generate relevant baseline information for Kano industrial estate.

Key words: Assessment, tannery, industrial effluent, Kano

INTRODUCTION

The direct discharge of effluents from tanneries into bodies of water has become a growing environmental problem. Most of these wastewaters are extremely complex mixtures containing inorganic and organic compounds (Fu *et al*., 1994). The tannery operation consists of converting the raw hide or skin into leather, which can be used in the manufacture of a wide range of products. Consequently, the tanning industry is a potentially pollution-intensive industry. Chemical impurities mostly comprise of the following dissolved substance: - (a) inorganic salt cations such as Fe^{2+}, Zn^{2+}, Cu^{2+}, Ca^{+}, Na^{+}, etc., anion such as So_4^{2-}, No_3^{-}, Po_4^{3-}; organic parameters such as Dissolved Oxygen (DO), Total Dissolved Solid (TDS) (Bosnic *et al*., 2000).

Industrial pollution is one of the problems presently facing Nigeria and several efforts are being vigorously pursued to control it at various industries spanning length and breadth of the country. This is to ensure that Nigerians live in a disease free environment. Effluents generated by the industries are the major sources of pollution. Contaminated air, soil and water by effluents from the industries are associated with heavy disease burden (WHO, 2002). Some heavy metals contained in these effluents (either in free form in the effluents or adsorbed in the suspended solids) from the industries have been found to be carcinogenic (Tamburlini *et al*., 2002) while other chemicals equally present are poisonous depending on the dose and exposure duration (Kupechella and Hyland, 1989). These chemicals are not only poisonous to humans but also found toxic to aquatic life (WHO, 2002) and they may result in food contamination (Novick, 1999). In addition to the above mentioned pollutants, plant nutrients such as phosphates and nitrates are pollutants because huge quantities enter the hydrosphere in runoffs from industrial effluents (Matsuo *et al*., 2001). In presence of other favourable abiotic factors such as temperature, pH, sunlight, a little over 0.01 mg L^{-1} phosphates and 0.1 mg L^{-1} nitrate speed micro-organism growth and thereby greatly accelerating eutrophication of natural waters (Matsuo *et al*., 2001).

The objective of this study was to assess the levels of pH, redox potential (Eh), DO, TDS nitrate, sulphate, phosphate and some heavy metals in tannery effluent from kano industrial area, Kano metropolis, Kano State Nigeria.

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MATERIALS AND METHODS

During this study, five tanneries were sampled for analysis, which included Challawa Tannery, Great Northern Tannery, Hafawa Enterprise (Tannery), Tannorth Tannery Limited and Unique Leather Finishing in Bompai, Sharada and Challawa Industrial Estate, Kano state, Nigeria. Their effluents were monitored through regular monthly grab sample collections for fourteen between the periods of September to December 2005. Grab samples were collected thrice a week. The samples were taken during the period of heaviest activity corresponding to the highest volume discharge. The fieldwork involved taking samples at points at which effluents discharge into drains for analyses.

There was a need for sample preservation and HACH (1997) recommended methods were used. All field meters and equipment were checked and calibrated according to the manufacturers specifications. The pH meter was calibrated using HACH (1997) buffers of pH 4.0, 7.0 and 10.0; Total Dissolved Solid (TDS) meter was calibrated using the potassium chloride solution provided by the manufacturer (HACH, 1997). Dissolved Oxygen (DO) meter was calibrated prior to measurement with the appropriate traceable calibration solution of (5% HCl) in accordance with the manufacturers instruction. The spectrophotometers (HACH DR2010) for anions determination were checked for malfunctioning by passing standard solutions of all the parameters to be measured; Blank samples (deionized water) were passed between every three measurements of effluent samples to check for any eventual contamination or abnormal response of equipment.

The dependent variables analyzed were pH, Eh, temperature, dissolved oxygen, total dissolved solid, nitrate, sulphate, phosphate and heavy metals concentration. Standard methods were followed in determining the above variables (APHA, 1998) Sample measurements were determined in sixteen replicate. *In situ* measurements for some of the parameters pH, Eh and temperature (°C) were measured using WTW pH Electrode SenTix 41. Dissolved oxygen was measured with Jenway Model 9070 waterproof DO meter whileTDS was determined by using a C0150 conductivity meter. The concentration of sulphate, nitrate and phosphate were determined using a DR/2010 HACH Portable Data Logging Spectrophotometer. The concentration of phosphate in the samples were determined using the ascorbic acid method by reacting it with added reagent containing molybdate and an acid to give a blue coloured complex (HACH, 1997).

Nitrate as N was determine by the cadmium metal method (HACH, 1997). The cadmium metal in the added reagent reduced all nitrate in the sample to nitrite. While sulphate was determined by using Sulfa Ver Standard Methods (HACH, 1997).

Heavy metal (copper, cobalt chromium, iron, zinc, manganese and lead) were determined using Atomic Absorption Spectrophotometer (AAS, Unicom 969). The effluent samples were digested as follows. One hundred cubic centimeter of the sample were transferred into a beaker and 5 mL concentrated HNO_3 were added. The beaker with the content was placed on a hot plate and evaporated down to about 20 mL. The beaker was cool and another 5 mL concentrated HNO_3 was also added. The beaker was covered with watch glass and returned to the hot plate. The heating was continued and then small portion of HNO_3 was added until the solution appeared light coloured and clear. The beaker wall and watch glass were washed with distilled water and the sample was filtered to remove some insoluble materials that could clog the atomizer. The volume was adjusted to 100 cm^3 with distilled water (Radojevic and Bashkin, 999). Determination of heavy metals in the effluent samples was done using Atomic Absorption Spectrophotometer (AAS, Unicom 969) as described in the manufacturers instruction manual.

Results were subjected to analysis of variance using the general linear models (Proc GLM) procedure of the statistical analysis system program package. Proc Univariate procedure was carried out on residuals to support the assumptions of normality made by the researchers. Where a significant Fisher test was observed, treatment means were separated using the Least Significant Difference at $p<0.05$.

RESULTS AND DISCUSSION

Mean concentration of metals; Co, Co, Zn, Mn, Pb, Fe, Cr, are shown in Table 1. Generally the mean concentration of metals differed significantly $p<0.05$. The concentration of Cu however did not significantly differ between Tanneries. Concentration of Co in Challawa Tannary, Great Northern tannery and Hafawa Enterprise Tannery were not statistically significantly.

Concentrations of Iron (1.23±0.01 to 0.16±0.01 mg L^{-1}); Manganese (0.31±0.04 to 0.63±0.01 mg L^{-1}); Zinc (0.35±0.01 to 1.21±0.01 mg L^{-1}) were all below the maximum permissible limits set by FEPA, (1991), with exception of Tannorth Tannery.

Levels of chromium (1.56±0.01 to 1.20±0.13 mg L^{-1}) were higher than the maximum permissible limits set by FEPA (1991) for all the tanneries studied. These high concentrations of chromium in all the tanneries are probably due to the chromium salt (chromium sulphate salt) used for tanning. The low values of Co, Cu and Mn

Table 1: Concentrations of heavy metals in different tannery effluent from Kano Metropolis, Kano State, Nigeria between the periods of September-December 2006

	Concentrations (mg L^{-1})						
Industry	Cu	Co	Zn	Mn	Pb	Fe	Cr
Challawa tannery	0.14 ± 0.04^{a}	0.21 ± 0.01^{a}	0.53 ± 0.03^{a}	0.31 ± 0.04^{a}	0.51 ± 0.02^{a}	0.27 ± 0.05^{a}	1.33 ± 0.01^{a}
Great northern tannery	0.18 ± 0.04^{b}	0.20 ± 0.02^{a}	0.59 ± 0.01^{b}	0.41 ± 0.01^{b}	0.23 ± 0.01^{b}	0.39 ± 0.01^{b}	1.14 ± 0.01^{b}
Hafawa enterprise (Tannery)	0.16 ± 0.02^{c}	0.21 ± 0.01^{a}	0.35 ± 0.01^{c}	0.63 ± 0.01^{c}	1.06 ± 0.01^{c}	0.58 ± 0.01^{c}	1.56 ± 0.06^{c}
Tannorth tannery limited	0.31 ± 0.01^{d}	0.23 ± 0.05^{b}	0.65 ± 0.02^{d}	0.61 ± 0.01^{d}	0.42 ± 0.01^{d}	1.23 ± 0.01^{d}	1.02 ± 0.01^{d}
Unique leather finishing	0.34 ± 0.24^{d}	0.13 ± 0.01^{c}	0.98 ± 0.01^{e}	0.38 ± 0.15^{e}	1.92 ± 0.30^{e}	0.16 ± 0.01^{e}	1.20 ± 0.13^{e}

The values given in the table above are means of replicate values (n = 42), Within columns, means with different letter(s) are statistically significant, $p<0.05$

Table 2: Characteristics of Effluents from Tannery Industries Kano Metropolis, Kano State, Nigeria between the Periods of September-December 2006

	Concentrations (mg L^{-1})							
Industry	pH	Eh $_{(m/volt)}$	T (°C)	DO	TDS	SO_4^{2-}	NO_3-$^{-}$	PO_4^{3-}
Challawa tannery	9.32 ± 0.30^{a}	-141.6 ± 14.3^{a}	31.44 ± 1.32^{a}	23.08 ± 0.80^{a}	661.3 ± 11.24^{a}	269.3 ± 5.34^{a}	171.6 ± 1.55^{a}	4.31 ± 0.14^{a}
Great northern tannery	9.61 ± 0.01^{b}	-155.5 ± 0.58^{b}	30.00 ± 0.05^{a}	24.85 ± 0.06^{b}	1281.1 ± 0.96^{b}	579.2 ± 5.68^{b}	159.4 ± 5.53^{b}	0.21 ± 0.02^{b}
Hafawa enterprise (tannery)	8.72 ± 0.23^{c}	-104.6 ± 2.87^{c}	30.25 ± 0.45^{a}	16.95 ± 0.79^{c}	889.6 ± 16.60^{c}	682.6 ± 2.25^{c}	104.8 ± 1.91^{c}	1.71 ± 0.13^{c}
Tannorth tannery limited	8.69 ± 0.45^{c}	-536.2 ± 11.61^{d}	30.45 ± 0.51^{a}	26.60 ± 1.08^{d}	646.4 ± 14.06^{d}	577.1 ± 6.89^{b}	150.4 ± 3.76^{d}	0.22 ± 0.03^{b}
Unique leather finishing	7.64 ± 0.24^{d}	-100.2 ± 1.86^{e}	30.31 ± 0.48^{a}	27.44 ± 0.71^{e}	65.4 ± 13.87^{e}	271.6 ± 1.46^{b}	13.6 ± 1.32^{e}	4.49 ± 0.22^{e}

Units are in mg L^{-1} unless pH, Eh and temperature. The values given in the table above are means of replicate values (n = 42), Within columns, means with different letter(s) are statistically significant, $p<0.05$, Units are in mg L^{-1} unless Ph, Eh and temperature

might be due to the fact that these metals are not principle sources of tannery effluent

Lead concentration in tanneries effluents were within acceptable limits of FEPA, (1991); with the exception of Hafawa enterprise and Unique leather finishing tannery. Mean concentrations of copper in all the tanneries studied were below guideline values for discharged of tannery effluent into rivers.

Temperatures in tanneries studied ranged between 30.00±0.05 to 31.44±.32°C (Table 2) and were below the limit set by the Federal Environment Protection Agency (FEPA, 1991).

The effluent pH differed significantly between tanneries. However, the effluent pH from challawa tannery and great northern tannery did not differ significantly.

The pH of the effluent discharged into rivers from all the tanneries under study were within the maximum permissible limits of pH 6.0-9.5 (Table 2). The pH of the effluent affects the availability of plant nutrients and heavy metals and growth of algae and micro-organisms. These effluents were basic in nature, which might be attributed to the salts the tanneries are using for tanning. The Eh values were within the safe limits for effluent discharged into rivers.

Concentration of total dissolve solid in the entire tannery varied between 661.4±11.24 to 1281.1±0.96 mg L^{-1} (Table 2). These values were relatively low and were significantly below the maximum permissible limits set by FEPA and WHO for the discharged of tannery effluent into rivers. DO contents in all the sampled point were not within the safety limits for maintenance of aquatic life of 5.00 mg L^{-1}.

Mean sulphate levels in the entire tannery effluent varied between 269.3±5.34 to 682.6±2.25 mg L^{-1}. The sulphate levels differed significantly among the tanneries (Table 2). Hafawa enterprise, Great northern tannery and tannorth tannery effluent had significantly high sulphate levels compared to challawa tannery and unique leather finishing and were significantly above the maximum permissible limits for the discharged of tannery effluent into rivers, (WHO, 2002). The South Africa quideline for sulphate in effluent is 0.2 mg L^{-1}, this limit was exceeded. These high values of sulphate are not surprising because sulphates are compounds of tannery effluent, emanating from the use of sulphuric acid or product with high sodium sulphate content. These high concentrations of sulphate in all the tanneries were also as a result of many auxiliary chemicals containing sodium sulphate as a by-product of the manufacturer or chrome tanning powders containing high levels of sodium sulphate (Bosnic *et al*., 2000).

Nitrate values were significantly higher in all the tannery effluent studied. The effluent nitrate values ranged from 104.8±1.91 to 171.6±1.55 mg L^{-1}. These values were higher than the standard values for the discharged of tannery effluent into rivers. These high levels of nitrate might 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) (Bosnic *et al*., 2000).

The phosphate levels also differed significantly among the five tanneries.

The effluent from challawa tannery and unique leather finishing had significantly higher phosphate values than hafawa enterprise, tannorth tannery and great northern tannery. These values were lower than the maximum permissible limits (WHO, 2002). The result is in line with the work of Uzo *et el.* (2006), analyst tannery effluent from Challawa industrial estate Kano, Nigeria. From the finding the concentration of the parameters were higher than the limits set by the FEPA for the discharged of industrial effluent by tannery sector.

Monthly variations of heavy metals in the tanneries under study (Challawa tannery, Great Northern tannery, Hafawa tannery, Tannorth tannery and Unique leathern finishing) are shown in Fig. 1-5, respectively. The values during the monthly sampling periods were between 0.01 to 0.60 mg L^{-1}, the levels of chromium was high in September to December when compared to other metals with exception of Tannorth tannery (Fig. 4) were iron shows high concentration than other metals. High values of chromium were observed in the month of December in the entire tanneries. On the other hand the levels of other metals (Cu, Co, Fe, Mn, Zn and Pb) were minimum in September to December. The high values of chromium when compared to other metals might be attributed to the use of chromium salts for tanning processes (Bajza and Vrcek, 2001). The relatively high concentrations of iron (Fig. 4) obtained when compared to other metals might be due to the fact that some of the chemicals used in the tanning process contain high levels of iron, while the low

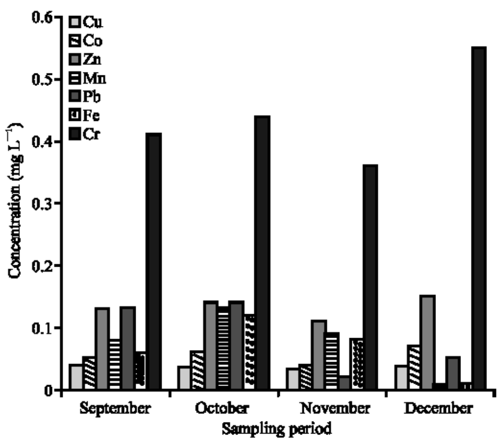

Fig. 1: Monthly variation of heavy metals in industrial effluent from Challawa tannery

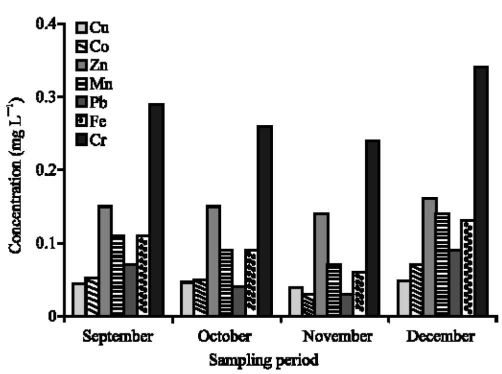

Fig. 2: Monthly variation of heavy metals in industrial effluent from Great Northern Tannery

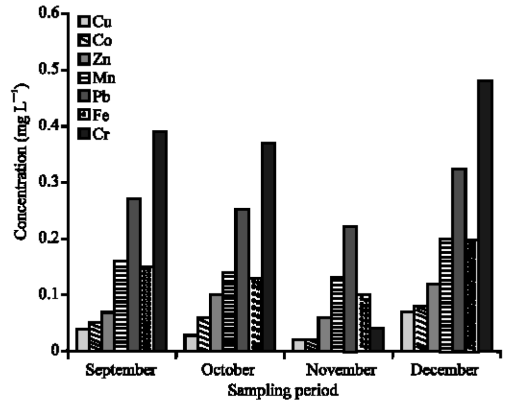

Fig. 3: Monthly variation of heavy metals in industrial effluent from Hafawa Enterprise

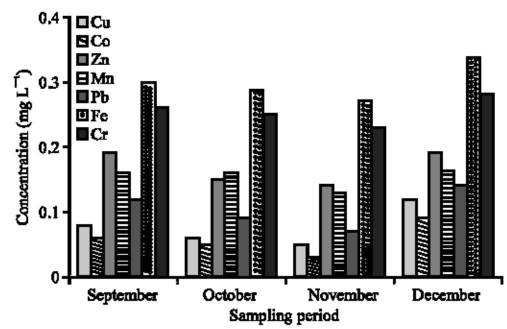

Fig. 4: Monthly variation of heavy metals in industrial effluent from Tannorth Tannery Limited

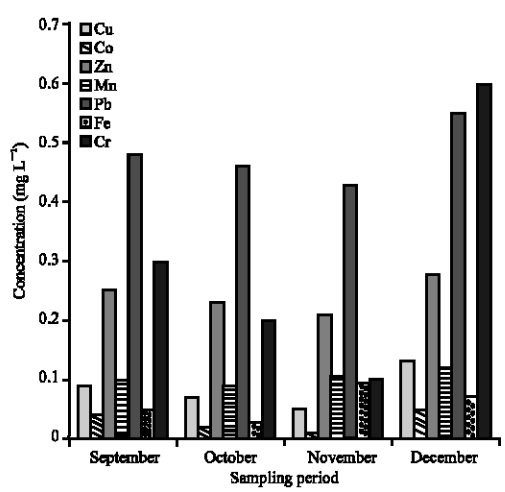

Fig. 5: Monthly variation of heavy metal in industrial effluent from Unique Leather Finishing

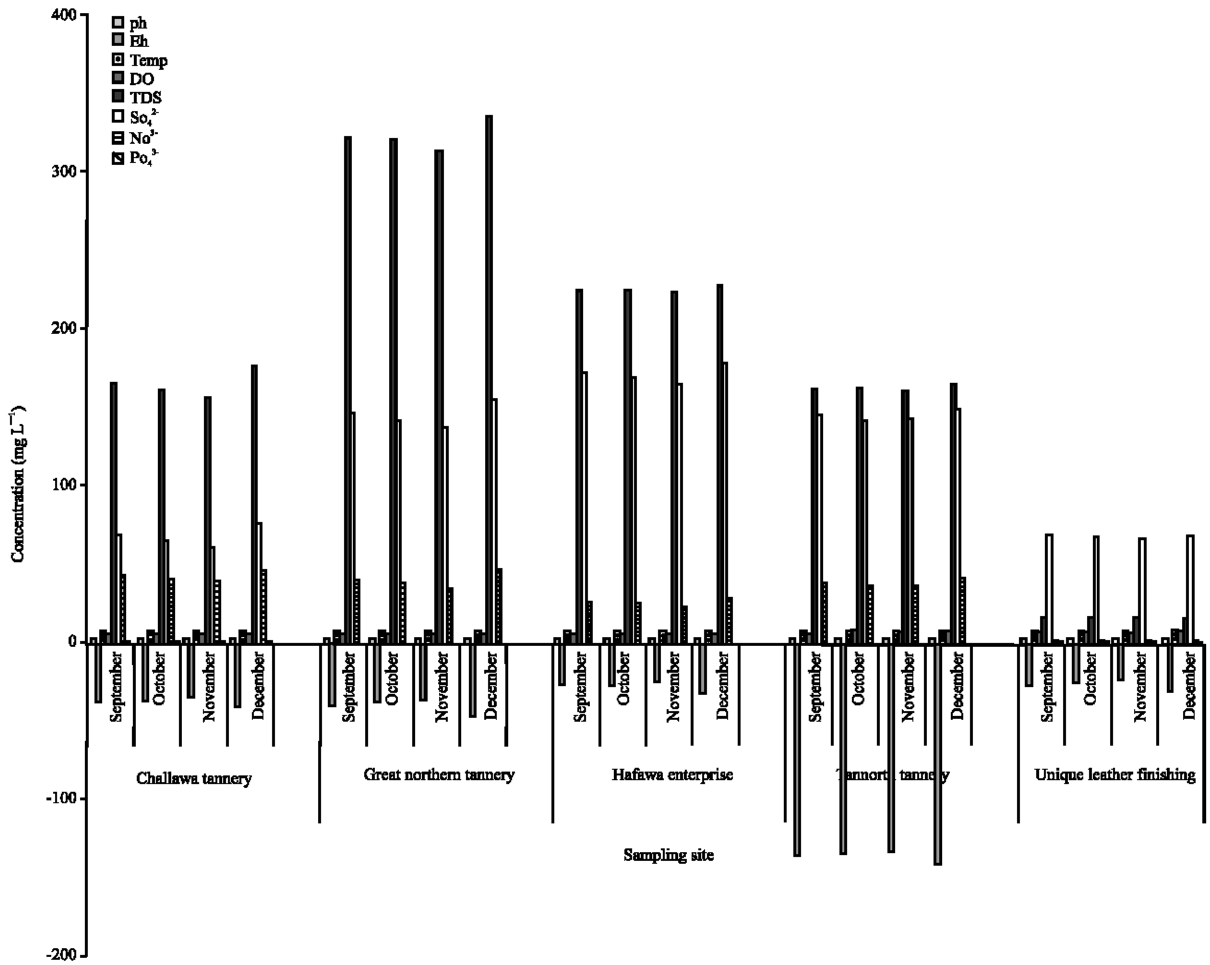

Fig. 6: Monthly Variations of some physio-chemical parameters in industrial effluent from different tannery

values of other metals might be attributed to the fact that the chemicals used in the tanning process contain low amount of these metals. Concentration of heavy metals in industrial effluent from the entire tanneries fell within the range set up by Federal Environmental Protection Agency (FEPA) Nigeria and WHO allowed for the discharged of tannery effluent into river.

The monthly variations of some physicochemical parameters (pH, Redox potential (Eh), Temperature, Dissolved oxygen, total dissolved solid, sulphate, nitrate and phosphate) in industrial effluent from the five tanneries are presented in Fig. 6. The monthly variation of these parameters shows that levels of total dissolved solid, sulphate and nitrate were highest in all tanneries studied. Levels of these parameters were highest in Great northern tannery while Unique leather finishing shows the lowest values. High values for sulphates in the entire tannery might be attributed to the fact that sulphates are compounds of tannery effluent emanating from the use of sulphuric acid or product with a high sodium sulphate content. (Bosnic *et el*., 2000). These high levels of nitrate might be as a result of several components in tannery effluent containing nitrogen as part of the chemical structure (Bosnic *et al*., 2000). Total Dissolved Solid (TDS) in the other hand might be due to the presence of high concentration of TDS and Turbidity from suspended solids, which originate from all stages of leather making. These comprise fine leather particles, residues from various chemical discharges and reagents from different waste liquors.

High redox potential (Eh) value was observed in Unique leather finishing, while a low value was observed in Tannorth tannery. The overall negative value in the tannery wastewater show that this environment is a reducing one.

The monthly variations of the physio-chemical parameter in this environment fell within the range set by FEPA and WHO for discharge of tannery effluent into water bodies.

CONCLUSION

It is therefore concluded that all the tanneries are the major sources of high chromium, sulphate, nitrate and dissolved oxygen discharged. While tannorth tannery could be a potential sources of high Iron in this area. High concentration of lead was also observed in Hafawa enterprise and Unique leather finishing. The concentration of Co, Cu, Mn, pH, temperature, Total dissolved solid and phosphate in all the tanneries effluent were generally below the maximum permissible values. The monthly variations of heavy metals in the entire tannery fell within the range set up by FEPA and WHO for the discharged of tannery effluent into river. Mean concentration of chromium, iron, sulphate, nitrate and dissolved oxygen levels should be monitored strictly by relevant authorities in order to prevent environmental pollution and reduce health hazards caused by pollution.

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