POLLUTANT LEVELS IN EFFLUENT SAMPLES FROM TANNERIES AND TEXTILES OF KANO INDUSTRIAL AREAS, NIGERIA

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ABSTRACT

Effluent samples from tanneries and textile industries from Kano industrial area of Challawa, Bompai and Sharada industrial area were collected on quarterly basis from June to September, 2007 (Rainy season), November, 2007 – February, 2008 (Harmattan season) and March – May, 2008 (Dry season) to reflect the seasonal factors. Effluents from ten industries were sampled and determined for physicochemical parameters. The physicochemical pollutants indicators determined include; Biological oxygen demand (BOD) and Chemical oxygen demand (COD) which all depend on the concentration of dissolved oxygen (DO) in effluent samples. Anions and trace elements were also determined. The above parameters were determined using standard procedures. From the results of the study, the concentrations of BOD, COD, DO, nitrate, nitrite, sulphate, phosphate, chloride and heavy metals were higher than the limits set by WHO for the discharged of tanneries and textile effluents into river. Result of analysis of variance (ANOVA) showed that variations between some industries were statistically significant (p≤0.05), but there were no marked seasonal variation in all the industries studied. Based on the high levels of the above parameters, it can be suggested that regular monitory of pollutants in the tannery and textile effluent are necessary to ensure proper discharge of these effluents into receiving river.

KEY WORDS: Pollutants, Levels, Effluent, Tanneries, Textile, Industrial Areas, Kano

INTRODUCTION

Industrial pollution is a problem and there are attempts to control it. Effluents generated by industries are sources for pollution. Contaminated air, soil, and water by effluents from industries are associated with disease burden and this could be reasons for the current shorter life expectancy (WHO, 2002; 2003) when compared with developed nations. Heavy metals in industrial effluent have been found to be carcinogenic, while others are poisonous depending on the dose and exposure period (Kupchella and Hyland, 1989; WHO, 2002). These chemicals are poisonous to man and aquatic life resulting in food contamination (Novick, 1999; WHO, 2003). For example ammonia is harmful to fish and other aquatic organisms at concentrations of 10 - 50 µg/l, the sulphate in effluents is of environmental concern (WHO, 2002) because this may lead to poor air quality of an area. The same is applicable to pH if water available for human use is not of the required quality (WHO, 1993).

Textile industry can be classified into three categories viz., cotton, woolen, and synthetic depending upon the raw materials used. The water consumption and wastewater generation from a textile industry depend upon the processing operations employed during the conversion of fiber to textile fabric. Textile industries are major sources of these effluents due to the nature of their operations, which require water that results in high wastewater generation (Ghoreishi and

Haghighi, 2003). The wastewater from a textile industry is characterized by high BOD, COD, colour, and pH (SDPI, 1995). High BOD levels in the untreated wastewater can cause rapid depletion of dissolved oxygen if directly discharged into the surface water. Effluents with high COD are toxic to biological life (Uzo et al., 2006). The high alkalinity and traces of chromium adversely affect the aquatic life and also interfere with the biological treatment process (EPA, 2003f and p).

The textile industry is distinguished by raw materials used which determine the volume of water required and hence the wastewater generated. Production may be from raw cotton and synthetic materials. In this type of production, slashing, bleaching, mercerizing, and dyeing are the activities where wastewater generation containing high biological oxygen demand, chemical oxygen demand, total dissolved solid, total suspended solid, oil and grease, pH, anions, temperature, colour and heavy metals are discharged with adverse effects on biological activity in water environment and man (Talbot, 1979). Specific water use in the textile industries varies from 60-400 l/kg of fabric, depending on the type of fabric (PRG, 1998).

Leather tanning and textile operations support leather shoe factories that make sandals, police boots, leather belt and bags providing finished export products and employment. There have been challenging issues regarding, resolving environmental pollution of effluents from these industries in Challawa, Sharada and Bompai industrial estates of Kano state, Nigeria (Felsner, 2003).

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Though there are several tanneries in Kano only two had functional upgraded primary treatment plant (PTP), (Felsner, 2003).

Kano (Lat. 11° 59m 18.3s N, Long 08° 32m 05.8s E) 418meters above sea level is located in Kano State and occupies a central position in Northern Nigeria. It is one of the developed industrial cities in Nigeria. Tannery and textile are some of the dominating industries and this could be one of the reasons for her high population density (Olanrewaju, 2001). Eventually the effluent from these textile and tannery operations is discharged onto land and into water bodies without treatment. In view, of the negative impact of this effluent on the environment, the present study is aimed at determining the levels of physicochemical pollutant indicators in effluent samples from textile and tanneries industries within the study areas.

MATERIALS AND METHODS

Sampling was from three industrial areas of Kano metropolis viz Challawa, Sharada and Bompai. Effluents from ten industries in these areas were studied with emphasis on tannery and textile industries. The ten industries comprise two textile and eight tanneries, they discharge their effluents into canals, which converge at a point and flow into River Challawa. Samples were collected at the point of discharge from each industry into the discharge channel.

Sample Collection

Effluent samples were collected in plastic containers previously cleaned by washing in non-ionic detergent, rinsed with tap water and later soaked in 10% $\rm HNO_3$ for 24 hours and finally rinsed with deionised water prior to usage. The samples were labeled and transported to the laboratory, stored in the refrigerator at about $\rm 4^{\circ}C$ prior to analysis.

Determination of Organic and Anions Pollutant Indicators

Dissolved oxygen (DO) of the effluent samples was determined using Jenway Model 9070 waterproof DO meter, while the biochemical oxygen demand (BOD) determination of the water sample in mg/l was carried out using the Standard Methods (1976). The dissolved oxygen content was determined before and after incubation. Sample incubation was for 5 days at 20°C in BOD bottle and BOD₅ was calculated after the incubation period. Determination of chemical oxygen

demand (COD) was carried out according to the method described by Ademoroti (1996). COD was determined after oxidation of organic matter in strong tetraoxosulphate VI acid medium by $K_2Cr_2O_7$ at $148^{\circ}C$, with back titration.

Determination of Heavy Metals in Effluent Samples

The effluent samples were digested according to (Radojevic and Bashkin, 1999). A blank sample was digested so as to allow a blank correction to be made. This was done by transferring 100ml of distilled water into a beaker and digested as described above.

Determination of Cu, Zn, Co, Mn, Mg, Fe, Cr, Cd As, Ni and Pb were made directly on each final solution using Perkin-Elmer Analyst 300 Atomic Absorption Spectroscopy (AAS) as described by Floyd and Hezekiah (1997).

Determination of Some Anions in Effluent Samples

The concentration of nitrate, nitrite, sulphate and phosphate were determined using a DR/2010 HACH Data Logging Spectrophotometer. spectrophotometers 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 water samples to check for any eventual contamination or abnormal response of equipment. Nitrate as nitrogen was determined by the cadmium reduction metal method 8036 (Standard methods, 1976., DWAF, 1992). The cadmium metal in the added reagent reduced all nitrate in the sample to nitrite; while sulphate was determined by using Sulfa Ver methods 8051 (Standard methods, 1976., DWAF, 1992).

In the determination of chloride, one hundred (100) milliliters of the water sample was measured into a 250ml conical flask and pH was adjusted to 8 with 1 M NaOH. One ml of K_2CrO_4 indicator was then added and titrated with the $AgNO_3$ solution. A blank titration was carried out using distilled water. Chloride (mg/l) was calculated according to (Ademoroti, 1996).

RESULTS AND DISCUSSION

The mean concentration of dissolved oxygen (DO) in tanneries and textile effluent for each seasons are as presented in Table 1. Dissolved oxygen values were consistently high in all the industries and during all the seasons sampled.

Table 1: Mean Seasonal Variation of Dissolved Oxygen (Mg/L) of Industrial Effluents From Different Industries Within Kano Industrial Areas between the Periods of 2007-2008

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INDUSTRIES	RAINY SEASON	HARMATTAN PERIOD	DRY SEASON
	(JUNE-SEPTEMBER)	(November-February)	(MARCH-MAY)
FATA TANNARY	34.42 ^{ab} ±1.43	33.12 ^{ab} ±1.71	32.23 ^{ab} ±1.30
MAMUDA TANNARY	32.33 ^{aa} ±1.54	35.21 ^{aa} ±1.63	36.12 ^{aa} ±2.73
MARIO JOSE TANNARY	35.21 ^{ab} ±2.51	33.99 ^{ab} ±2.57	34.66 ^{ab} ±1.34
KANOTAN TANNARY	31.23 ^{aa} ±1.43	32.43 ^{ab} ±1.50	33.44 ^{ab} ±1.43
MUAZA TANNARY	38.22 ^{ac} ±1.17	37.46 ^{ac} ±1.47	36.45 ^{aa} ±1.76

GOD LITTLE TANNARY	29.42 ^{aa} ±1.40	31.23 ^{ab} ±2.60	30.26 ^{ab} ±1.36
TANNORTH TANNARY	32.44 ^{aa} ±1.06	35.22 ^{aa} ±2.11	33.17 ^{ab} ±1.36
UNIQUE LEATHER FINISHING	30.54 ^{aa} ±1.72	31.11 ^{ab} ±1.32	32.55 ^{ab} ±1.52
HOLBORN TEXTILE	27.33 ^{ad} ±1.42	28.24 ^{ad} ±1.22	28.64 ^{ac} ±1.83
AFRICAN TEXTILE	33.88 ^{aa} ±2.37	33.24 ^{ab} ±1.32	31.39 ^{ab} ±1.68

Mean with different letters are statistically different, P< 0.05

First superscript = between seasons

Second superscript = between industries

The mean DO concentrations of effluent in all the industries for rainy season (June - September, 2007) ranged between 27.33±1.42 to 38.22±1.17 mg/l, for Harmattan period (November 2007 – February 2008) 28.24±1.22 to 37.46±1.47 mg/l and .64±1.83 to 36.45±1.76 mg/l for dry season (March - May 2008). Muaza tannery recorded relatively higher dissolved oxygen values, while Holborn textile showed the least values in all the seasons sampled. These variations might be due to chemicals used in tannaries and textile industries which increase the organic matter leading to low DO values. Despite these variations in dissolved oxygen between industries, they were no marked or distinct variations for dissolved oxygen between seasons, indicating that the activities of these industries remain almost constant throughout the seasons.

Analysis of variance (ANOVA) indicate that variation between seasons were not statistically

significantly (p>0.05). Though fluctuations in DO levels were recorded within industries, all the values obtained were above the WHO (1984) and USEPA (1999) permissible limit of 4mg/l and 5mg/l for the discharged of effluent tanneries and textile industries into river. DO contents in all the sampling points were above the safety limits for maintenance of aquatic life of 5.00mg/l.

The mean concentration of biological oxygen demand (BOD) of the effluent based on industries and seasons are as showed in Table 2. The concentrations of BOD in the rainy season (June - September, 2007) ranged between 594.67±52.91 to 672.70±33.72 mg/l., 585.67±42.83 to 669.20±53.72 mg/l for Harmattan period (November 2007 – February 2008) and 590.47±53.71 to 664.30±33.72 mg/l for dry season (March – May 2008).

Table 2: Mean Seasonal Variation of Biological Oxygen Demand (Mg/L) of Industrial Effluents from Different Industries within Kano Industrial Areas between the Periods of 2007-2008

INDUSTRIES	RAINY SEASON (JUNE-SEPTEMBER)	HARMATTAN PERIOD (November-February)	DRY SEASON (MARCH-MAY)
EATA TANINADV	594.67 ^{ab} ±52.91	585.67 ^{ab} ±42.83	,
FATA TANNARY	594.67 ±52.91	585.67 ±42.83	590.47 ^{ab} ±53.71
MAMUDA TANNARY	638.00 ^{aa} ±43.31	644.00 ^{aa} ±53.33	632.60 ^{aa} ±47.01
MARIO JOSE TANNARY	639.33 ^{aa} ±46.23	647.32 ^{aa} ±42.13	637.23 ^{aa} ±56.23
KANOTAN TANNARY	621.67 ^{ac} ±73.28	627.11 ^{ac} ±64.28	625.47 ^{ac} ±63.28
MUAZA TANNARY	629.00 ^{ac} ±61.65	635.00 ^{ad} ±66.15	630.10 ^{ad} ±42.65
GOD LITTLE TANNARY	612.70 ^{ad} ±87.96	616.75 ^{ae} ±77.26	609.80 ^{ae} ±77.96
TANNORTH TANNARY	622.30 ^{ac} ±61.13	625.20 ^{ac} ±48.43	627.37 ^{ac} ±66.33
UNIQUE LEATHER FINISHING	623.70 ^{ac} ±71.68	630.60 ^{ac} ±56.68	633.71 ^{aa} ±51.68
HOLBORN TEXTILE	672.70 ^{ad} ±33.72	669.20 ^{af} ±53.72	664.30 ^{ae} ±33.72
AFRICAN TEXTILE	626.00 ^{ac} ±66.36	619.30 ^{ae} ±58.31	624.60 ^{ac} ±55.36

Mean with different letters are statistically different, P< 0.05

First superscript = between seasons

Second superscript = between industries

Table 3: Mean Seasonal Variation of Chemical Oxygen Demand (Mg/L) of Industrial Effluents From Different
Industries within Kano Industrial Areas between the Periods of 2007-2008

INDUSTRIES	RAINY SEASON	HARMATTAN PERIOD	DRY SEASON
	(June-September)	(November-February)	(March-May)
FATA TANNARY	2412.00 ^{ab} ±151.70	2422.00 ^{ab} ±155.11	2428.00 ^{ab} ±165.11
MAMUDA TANNARY	2399.00 ^{ab} ±143.50	2389.00 ^{ab} ±133.50	2391.00 ^{ab} ±146.50
MARIO JOSE TANNARY	3451.00 ^{aa} ±1910.00	3441.00 ^{aa} ±1810.10	3447.00 ^{a a} ±1710.23
KANOTAN TANNARY	3415.00 ^{aa} ±1848.00	3485.00 ^{aa} ±1848.03	3488.00 ^{aa} ±1858.33
MUAZA TANNARY	3484.00 ^{aa} ±1968.00	3474.00 ^{aa} ±1768.23	3479.00 ^{aa} ±1658.32
GOD LITTLE TANNARY	3438.00 ^{aa} ±1887.00	3458.00 ^{aa} ±1687.33	3459.00 ^{aa} ±1787.21
TANNORTH TANNARY	3444.00 ^{aa} ±1897.00	3454.00 ^{aa} ±1597.08	3449.00 ^{aa} ±1697.00
UNIQUE LEATHER FINIS	3418.00 ^{aa} ±1852.00	3422.00 ^{aa} ±1852.00	3419.00 ^{aa} ±1852.00
HOLBORN TEXTILE	3784.00 ^{ac} ±1234.00	3774.00 ^{ac} ±1334.00	3778.00 ^{ac} ±1434.22
AFRICAN TEXTILE	3419.00 ^{aa} ±1852.30	3423.00 ^{aa} ±1852.09	3426.00 ^{aa} ±1752.00

Mean with different letters are statistically different, P< 0.05

First superscript = between seasons

Second superscript = between industries

All the industries gave biological oxygen demand (BOD) values higher than the recommended tolerance level stipulated by FEPA for the discharged of tanneries and textile effluents into rivers (50mg/l). Holborn textile recorded relatively higher dissolved oxygen values of 584.67 ± 52.91 to 594.67 ± 52.91 mg/l, while Fata tannery showed the least values of 664.30 ± 33.72 to 672.70 ± 23.42 mg/l in all the seasons sampled. These values were higher than WHO standard of 20mg/l for effluent to be discharged into surface water.

The mean concentrations of chemical oxygen demand (COD) for all the industries and seasons are as shown in Table 3. The mean COD concentration of effluent in all the industries in the rainy season (June -September, 2007) ranged between 2399.00±143.50 to 3784.00±1234.12 mg/l., 2389.00±133.50 3774.00±1334.21 mg/l for Harmattan period (November 2007 - February 2008) and 2391.00±146.50 to 3778.00±1434 mg/l for dry season (March – may 2008). The values of COD were nearly uniform in all the industries studied based on seasons. Holborn textile recorded relatively higher COD values 3774.00±1334.21 to 3778.00±1434 mg/l, while Mamuda tannery showed the least values of 2389.00±133.50 to 2399.00 ±143.50 mg/l in all the seasons sampled. These values were higher than WHO, USEPA standard of 1000 mg/l for discharged of tanneries and textile effluent into surface water.

These high levels of BOD and COD values observed in all the industries may be due to high amount of organic matter from various chemicals used during the soaking, tanning and post tanning processing of hides and skins and chemicals used in textile industries for mercerizing, bleaching / scouring and yeing which include sodium sulphite, sodium bisulphate, sodium

chlorite, NaCl, H_2SO_4 , formic acid, sodium formate, sodium bicarbonate,

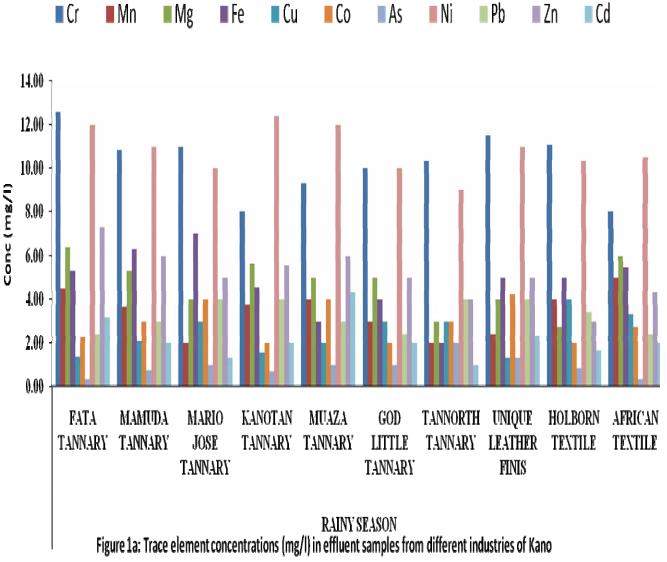
vegetable tannins, syntans, resins, polyurethane, dyes, fat emulsions, pigments, binders, waxes, lacquers and formaldehyde, sodium hypochlorite, C_{12} , NaOH, H_2O_2 , acids, surfactants, NaSiO₃ and sodium phosphate. It has been reported that only about 20% of the large number of chemicals used in the tanning process is absorbed by leather, the rest is released as waste (UNIDO, 2005), thereby increasing the levels of BOD in the effluent.

Result of analysis of variance (ANOVA) showed that variation between industries were statistically different (p<0.05) with exception of Holborn textile and Fata tannery, but there were no marked seasonal variation of BOD and COD in all the industries studied. These results show that the discharged of effluent and the activities by these industries remained almost constant throughout the sampling periods.

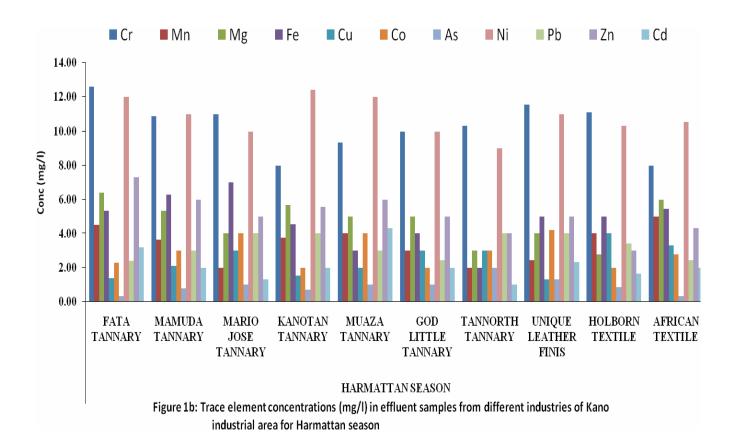
The results for heavy metals concentration in effluent samples from different industries and seasons are as presented in Figure 1a, b and c. The composition of heavy metals in the effluent samples ranged from 8.00 to 12.60 mg/l for Cr; 2.00 to 5.00 mg/l Mn; 2.77 to 6.40 mg/l Mg; 2.00 to 7.02 mg/l Fe; 1.33 to 4.00 mg/l Cu; 2.00 to 4.22 mg/l Co; 0.34 to 2.00 mg/l As, 9.00 to 12.44 mg/l Ni; 2.40 to 4.03 mg/l Pb; 3.00 to 7.33 mg/l Zn; and 1.00 to 3.20 mg/l Cd for rainy season (June -September, 2007) Figure 1a. 8.22 to 12.50 mg/l for Cr; 2.10 to 5.30 mg/l Mn; 2.97 to 6.20 mg/l Mg; 2.20 to 7.42 mg/l Fe; 1.39 to 4.10 mg/l Cu; 2.30 to 4.12 mg/l Co; 0.44 to 2.00 mg/l As, 9.20 to 12.56 mg/l Ni; 2.33 to 4.22 mg/l Pb; 3.20 to 7.11 mg/l Zn; and 1.20 to 3.14 mg/l Cd for Harmattan period (November 2007 - February 2008) Figure 1 b. 8.01 to 12.59 mg/l for Cr; 2.14 to 5.38 mg/l Mn; 2.92 to 6.20 mg/l Mg; 2.25 to 7.10 mg/l Fe; 1.29 to 4.16 mg/l Cu; 2.26 to 4.13 mg/l Co; 0.39 to 2.11 mg/l As,

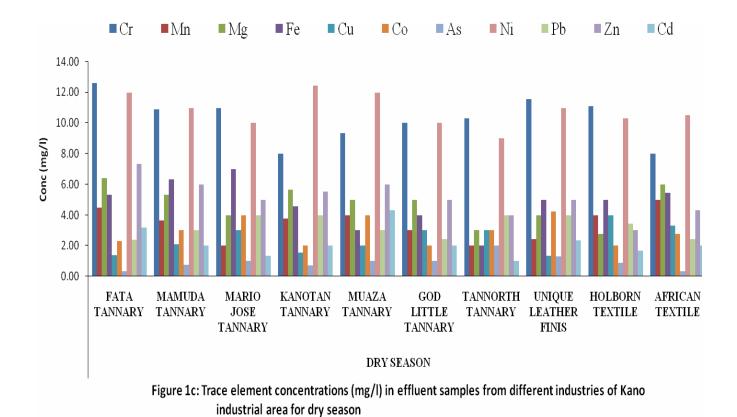
9.26 to 12.66 mg/l Ni; 2.33 to 4.32 mg/l Pb; 3.23 to 7.10 mg/l Zn; and 1.22 to 3.11 mg/l Cd for dry season (March - May 2008) Figure 1c. In general, the trend in heavy metal variability and mean concentrations in the effluent samples were Cr> Ni> Zn> Mg> Fe> Mn> Pb> Co> Cu> Cd> As, respectively. The values of heavy metals were nearly uniform in all the industries studied. These values were higher than WHO/USEPA standard of 0.1mg/l Cr; 00.10mg/l Ni; 1.0 mg/l Zn; 1.0mg/l Mg; 0.30 mg/l Fe; 1.0 mg/l Mn; 0.2 mg/l Pb; 1.00 mg/l Cu; 1.00 mg/l Co; 0.03 mg/l Cd and 0.10 mg/l As for the discharged of tanneries and textile effluent into surface water. These high values of heavy metals observed in

all the effluent may be due to the chemicals used by tanneries and textile industries which contain high concentration of these metals, chromium and other heavy metals are mainly found in waste from the chrome tanning process and other chemicals, it occurs as part of the retanning system and is displaced from leathers and fabric during retanning and dyeing processes. Result of analysis of variance (ANOVA) showed that variation between some industries were significantly different (p<0.05), but there were no marked seasonal variation in all the industries studied.



industrial area for rainy season





The mean seasonal variation of nitrate concentrations in the effluent samples from different industries within Bompai, Sharada and Challawa industrial estate are illustrated in Table 4, while levels of nitrite and phosphate are as presented in Tables 5 and 6 respectively. The mean nitrate concentration of effluent in all the industries in the rainy season (June - September, 2007) ranged between 59.22±3.22 to 95.24±3.29 mg/l., 58.32±2.52 to 93.22±1.23 mg/l for Harmattan period (November 2007 – February 2008) and 57.88±2.22 to 94.77±2.01 mg/l for dry season (March – May 2008), while the mean levels of nitrite in

industrial effluent from all the industries in the rainy season (June - September, 2007) ranged between 134.22±7.12 to 193.33±6.43 mg/l., 136.22±2.44 to 196.44±5.32 mg/l for Harmattan period (November 2007 – February 2008) and 137.22±3.17 to 192.44±7.02 mg/l for dry season (March – May 2008). The mean concentrations of phosphate in industrial effluent from all the industries in the rainy season (June - September, 2007) ranged between 16.44±3.76 to19.33±1.43 mg/l., 16.65±2.92 to 19.77±5.32 mg/l for Harmattan period (November 2007 – February 2008) and 16.65±1.11 to 19.93±2.02 mg/l for dry season (March – May 2008).

Table 4: Mean Seasonal Variation of Nitrate (Mg/L) in Industrial Effluents from Different Industries within Kano Industrial Areas between the Periods of 2007-2008

INDUSTRIES	RAINY SEASON	HARMATTAN PERIOD	DRY SEASON
	(JUNE-SEPTEMBER)	(November-February)	(MARCH-MAY)
FATA TANNARY	84.36 ^{ab} ±6.33	86.77 ^{ab} ±3.45	87.00 ^{ab} ±4.21
MAMUDA TANNARY	85.66 ^{ab} ±2.10	87.34 ^{ab} ±7.44	86.23 ^{ab} ±4.77
MARIO JOSE TANNARY	95.24 ^{aa} ±3.29	93.22 ^{aa} ±1.23	94.77 ^{aa} ±2.01
KANOTAN TANNARY	76.21 ^{ac} ±2.08	78.23 ^{ac} ±2.30	77.12 ^{ac} ±1.22
MUAZA TANNARY	83.12 ^{ab} ±1.54	84.06 ^{ab} ±2.10	81.43 ^{ab} ±3.59
GOD LITTLE TANNARY	74.22 ^{ac} ±2.45	73.06 ^{ac} ±1.03	72.00 ^{ad} ±3.22
TANNORTH TANNARY	76.56 ^{ac} ±1.03	77.23 ^{ac} ±4.20	76.21 ^{ac} ±2.12
UNIQUE LEATHER FINIS	59.22 ^{ad} ±3.22	58.32 ^{ad} ±2.52	57.88 ^{ae} ±2.22
HOLBORN TEXTILE	07 00 ⁸ b 0 40	07 00 ⁸ b 0 00	00 00 ⁸ b 0 00
AFRICAN TEXTILE	87.23 ^{ab} ±3.43	87.60 ^{ab} ±6.32	86.20 ^{ab} ±3.02
	78.13 ^{ac} ±1.76	80.00 ^{ac} ±2.43	79.05 ^{ac} ±3.11

Mean with different letters are statistically different, P< 0.05

First superscript = between seasons

Second superscript = between industries

Table 5: Mean Seasonal Variation of Nitrite (Mg/L) in Industrial Effluents from Different Industries within Kano Industrial Areas between the Periods of 2007-2008

INDUSTRIES	RAINY SEASON (JUNE-SEPTEMBER)	HARMATTAN PERIOD (November-February)	DRY SEASON (MARCH-MAY)
FATA TANNARY	145.21 ^{ab} ±4.13	146.43 ^{ab} ±3.25	144.32 ^{ab} ±6.43
MAMUDA TANNARY	134.22 ^{aa} ±7.12	136.22 ^{aa} ±2.44	137.22 ^{aa} ±3.17
MARIO JOSE TANNARY	174.22 ^{ac} ±5.34	176.32 ^{ac} ±4.32	175.23 ^{ac} ±5.01
KANOTAN TANNARY	165.54 ^{ad} ±3.08	164.00 ^{ad} ±7.30	166.54 ^{ad} ±6.22
MUAZA TANNARY	168.54 ^{ad} ±2.54	167.55 ^{ad} ±9.10	165.43 ^{ad} ±7.09
GOD LITTLE TANNARY	183.33 ^{ae} ±6.45	184.62 ^{ae} ±5.03	185.32 ^{ae} ±8.22
TANNORTH TANNARY	176.23 ^{ac} ±2.90	177.55 ^{ac} ±2.20	175.54 ^{ac} ±4.22
UNIQUE LEATHER FINIS	163.45 ^{ad} ±7.32	164.43 ^{ad} ±7.52	162.00 ^{ad} ±3.22
HOLBORN TEXTILE	193.33 ^{af} ±6.43	196.44 ^{af} ±5.32	192.44 ^{af} ±7.02
AFRICAN TEXTILE	188.34 ^{ae} ±0.76	186.65 ^{ae} ±3.92	187.44 ^{ae} ±5.11

Mean with different letters are statistically different, P< 0.05 First superscript = between seasons Second superscript = between industries

Table 6: Mean Seasonal Variation of Phosphate (Mg/L) in Industrial Effluents from Different Industries within Kano Industrial Areas between the Periods of 2007-2008

INDUIGEDIES		territie Ferious of 2007-2006	DDV 054001
INDUSTRIES	RAINY SEASON	HARMATTAN PERIOD	DRY SEASON
	(JUNE-SEPTEMBER)	(November-February)	(MARCH-MAY)
		-1-	-1-
FATA TANNARY	18.39 ^{ab} ±0.52	18.87 ^{ab} ±2.25	19.23 ^{ab} ±3.43
MAMUDA TANNARY	19.22 ^{ab} ±4.12	18.87 ^{ab} ±1.44	19.00 ^{ab} ±1.14
MARIO JOSE TANNARY	17.00 ^{ac} ±2.34	18.98 ^{ac} ±3.32	17.56 ^{ac} ±3.21
KANOTAN TANNARY	16.46 ^{ac} ±1.08	16.99 ^{ac} ±1.37	16.68 ^{ac} ±2.52
MUAZA TANNARY	18.11 ^{ab} ±2.54	18.65 ^{ab} ±1.10	18.45 ^{ab} ±1.09
GOD LITTLE TANNARY	19.22 ^{ab} ±1.45	19.00 ^{ab} ±2.03	19.43 ^{ab} ±1.22
TANNORTH TANNARY	18.43 ^{ab} ±2.90	18.56 ^{ab} ±2.20	18.91 ^{ab} ±4.22
UNIQUE LEATHER	17.77 ^{ac} ±3.32	17.65 ^{ac} ±2.52	17.32 ^{ac} ±1.22
FINIS			
HOLBORN TEXTILE	19.33 ^{ab} ±1.43	19.77 ^{ab} ±5.32	19.93 ^{ab} ±2.02
	10.00 ±1.40	10.77 = 20.02	10.000_
AFRICAN TEXTILE	16.44 ^{ac} ±3.76	16.65 ^{ac} ±2.92	16.65 ^{ac} ±1.11
/ 11 11 10 / 11 1 L/(IILL	10.77 ±0.70	10.00 ±2.02	10.00 ± 1.11

Mean with different letters are statistically different, P< 0.05

First superscript = between seasons

Second superscript = between industries

Mario Jose tannery recorded the highest concentration of nitrate (93.22±1.23 to 95.24±3.29 mg/l) in comparison to other industries under study throughout the seasons, while low nitrate level of 57.88±2.22 to 59.22±3.22 mg/l was observed in Unique leather finishing. For nitrite concentrations, Holborn textile recorded the highest concentration of 192.44±7.02 to 196.44±5.32 mg/l throughout the seasons, while Mamuda tannery shows the least concentrations of nitrite (134.22±7.12 to 137.22±3.17 mg/l). Phosphate levels were highest in

Holborn textile throughout the seasons (19.33±1.43 to 19.93±2.02 mg/l), while the least concentration was observed in African textile (16.44±3.76 to16.65±1.11 mg/l. The mean nitrate, nitrite and phosphate concentrations recorded for all the industries in this study were above the stipulated WHO/USEPA/FEPA tolerance limit of between 45 mg/l, 25 mg/l and 5 mg/l respectively for effluents to be discharged from tanneries and textile industries into river or stream. These high levels of nitrate, nitrite in the entire industries might be attributed to 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 mean concentrations of sulphate for all the industries and seasons are shown in Table 7. While the chloride for all the industries and seasons are shown in

Table 8. The mean sulphate concentration of effluent in all the industries in the rainy season (June - September, 2007) ranged between 545.34±2.32 to 978.13±11.76 mg/l., 552.22±2.47 to980.00±12.43 mg/l for Harmattan period (November 2007 - February 2008) and 548.31±3.22 to 976.05±13.11mg/l for dry season (March - may 2008). The concentrations of chloride ranged from 175.90±9.54 to 654.15±111.76 mg/l for rainy season (June - September, 2007)., 174.97±10.34 to 658.32±212.43 mg/l Harmattan period (November 2007 February 2008)., 176.45±15.01 to 636.12±233.11 mg/l for dry season (March - may 2008). African textile recorded relatively higher sulphate values, while Kanotan tannery showed the least values. These values were higher than the WHO, USEPA standard of 250 mg/l sulphate for the discharged of tanneries and textile effluent into surface water. The South African quideline for sulphate in effluent is 0.2 mg/l, this limit was exceeded. These high levels of sulphate observed in all the effluent may be due to the fact that sulphates are compounds of tanneries and textile effluent emanating from the use of sulphuric acid or product with high sodium sulphate content. These high concentrations of sulphate in all the tanneries and textile effluent may also be attributed to the fact that many auxiliary chemicals used in these industries contain sodium sulphate as a by-product of the manufacturer or chrome tanning powders containing high levels of sodium sulphate (Bosnic et al., 2000).

Table 7: Mean Seasonal Variation of Sulphate (Mg/L) in Industrial Effluents from different Industries within Kano Industrial Areas between the Periods of 2007-2008

	Industrial Areas between the	e Periods of 2007-2008	
INDUSTRIES	RAINY SEASON	HARMATTAN PERIOD	DRY SEASON
	(JUNE-SEPTEMBER)	(November-February)	(MARCH-MAY)
	·	•	
FATA TANNARY	834.22 ^{ab} ±6.33	838.23 ^{ab} ±3.45	841.12 ^{ab} ±12.21
	a b	a b	-h
MAMUDA TANNARY	812.32 ^{ab} ±5.35	815.22 ^{ab} ±7.14	810.34 ^{ab} ±8.34
MARIO JOSE TANNARY	943.23 ^{aa} ±12.23	948.34 ^{aa} ±10.21	942.23 ^{aa} ±14.53
KANOTAN TANNARY	545.34 ^{ac} ±2.32	552.22 ^{ac} ±2.47	548.31 ^{ac} ±3.22
KANOTAN TANNARY	545.34 ±2.32	552.22 ±2.47	548.31 ±3.22
MUAZA TANNARY	674.65 ^{ad} ±4.34	678.00 ^{ad} ±2.90	671.21 ^{ad} ±3.59
WOALATAWAKI	074.00 14.04	070.00 12.00	071.21 ±0.00
GOD LITTLE TANNARY	746.90 ^{ae} ±3.45	738.06 ^{ae} ±4.03	741.22 ^{ae} ±14.76
TANNORTH TANNARY	664.33 ^{ad} ±5.50	667.22 ^{ad} ±4.44	661.11 ^{ad} ±2.70
UNIQUE LEATHER FINIS	567.21 ^{ac} ±5.22	564.00 ^{ac} ±7.55	569.00 ^{ac} ±3.22
	ah .	a ab	ah ah
HOLBORN TEXTILE	878.00 ^{ab} ±6.43	874.20 ^{ab} ±8.32	876.20 ^{ab} ±7.82
A EDIO ANI TEVTILE	070 40 ^{af} 44 70	000 00 ^{af} . 40 . 40	070 05 ⁸ f . 40 44
AFRICAN TEXTILE	978.13 ^{af} ±11.76	980.00 ^{af} ±12.43	976.05 ^{af} ±13.11

Mean with different letters are statistically different, P< 0.05

First superscript = between seasons

Second superscript = between industries

Table 8: Mean Seasonal Variation of Chloride (Mg/L) in Industrial Effluents from different Industries within Kano Industrial Areas between the Periods of 2007-2008

INDUSTRIES	RAINY SEASON (JUNE-SEPTEMBER)	HARMATTAN PERIOD (November-February)	DRY SEASON (MARCH-MAY)
FATA TANNARY	314.12 ^{ab} ±34.09	311.00 ^{ab} ±32.11	322.21 ^{ab} ±22.92
MAMUDA TANNARY	253.11 ^{aa} ±11.10	247.32 ^{aa} ±12.00	249.54 ^{aa} ±13.83
MARIO JOSE TANNARY	287.04 ^{ac} ±16.32	286.03 ^{ac} ±15.43	288.00 ^{ac} ±12.65
KANOTAN TANNARY	223.11 ^{ad} ±10.21	227.26 ^{ad} ±14.54	229.00 ^{ad} ±21.21
MUAZA TANNARY	221.21 ^{ad} ±12.81	222.77 ^{ad} ±11.08	231.39 ^{ad} ±17.21
GOD LITTLE TANNARY	189.00 ^{ae} ±12.11	191.32 ^{ae} ±21.03	188.04 ^{ae} ±14.76
TANNORTH TANNARY	175.90 ^{ae} ±9.54	174.97 ^{ae} ±10.34	176.45 ^{ae} ±15.01
UNIQUE LEATHER FINIS	231.30 ^{ad} ±11.90	234.77 ^{ad} ±16.55	232.00 ^{ad} ±13.87
HOLBORN TEXTILE	621.12 ^{af} ±231.21	625.65 ^{af} ±211.10	623.33 ^{af} ±251.82
AFRICAN TEXTILE	654.15 ^{af} ±111.76	658.32 ^{af} ±212.43	636.12 ^{af} ±233.11

Mean with different letters are statistically different, P< 0.05

First superscript = between seasons

Second superscript = between industries

The values of chloride in all the industries under study were higher than the WHO standard of 150 mg/l for the discharged of tannery and textile effluent into rivers. The high values of chloride in the effluent might be due to the fact that chloride are introduced into tannery effluents as sodium chloride usually on account of the large quantities of common salt used in hide and skin preservation or the pickling process, being highly soluble and stable, they are unaffected by effluent

treatment and nature, thus remaining as a burden on the environment (Bhatia, 2005, Bosnic *et al.*, 2000).

Result of analysis of variance (ANOVA) showed that variation between industries were statistically significant (p<0.05) with exception of some industries, but there were no marked seasonal variation for nitrate, nitrite, phosphate sulphate and chloride in all the industries studied.

SUMMARY AND CONCLUSION

The levels of dissolved oxygen (DO), chemical oxygen demand (COD) and biological oxygen demand (BOD) in all the industries were found to be higher than the optimum ranged for the discharge of tannery and textile effluent into river and stream. High concentrations of heavy metals were observed to accumulate in all the effluent samples from tanneries and textile industries studied. The concentrations of sulphate, chloride, nitrate, nitrite and phosphate of effluent in all the industries sample studied were higher than the USEPA limits for the discharge of industrial effluent into river

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