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## Determination of Pollutant Levels in Mario Jose Tannery Effluents from Kano Metropolis, Nigeria

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**Abstract:** The uncontrolled releases of waste effluents to large water bodies have deleterious effects both on water quality and aquatic life. Kano, an industrial city in Nigeria has the largest number of tanneries in the country is facing the problems of impairment of water quality. Levels of heavy metals (Cu, Co, Zn, Mn, Pb, Fe and Cr) were determined using Atomic Absorption spectrophotometric methods. pH, Redox potential (Eh), Temperature, Dissolve Oxygen (DO), Total Dissolve Solid, sulphate, nitrate and phosphate were also determined. Results showed high levels of Cr ( $2.70 \pm 0.57$  to  $3.12 \pm 0.69$  mg L<sup>-1</sup>), Fe ( $1.21 \pm 0.13$  to  $1.61 \pm 0.41$  mg L<sup>-1</sup>) and these values were found to be significantly higher than the maximum permissible limits of FEPA ( $p < 0.05$ ). Levels of Mn, Cu, Zn, Pb and Co were within the minimum permissible limits for effluent discharged into rivers. Increases, in concentrations of heavy metals with distance from point source up to a distance of 400 metres were observed. While anion concentration decreased with distance from point source up to a distance of 400 m. Adherence to pollution control measures and effluent pre-treatment should be enforced in the industries.

**Key words:** Tannery effluent, pollutant, heavy metals

### INTRODUCTION

The impairment of water quality due to introduction of industrial pollutants is a major problem faced by big industrial cities. Wastewater from industries includes employees' sanitary waste, process waste from manufacturing, wastewater and relatively uncontaminated water from heating and cooling operations. The processing wastewater is a major area of concern (Glynn, and Gary, 1996). These may vary widely with the type of industry.

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<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Ca<sup>+</sup>, Na<sup>+</sup>; etc; anion such as SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>; organic parameters such as DO, TDS (APHA *et al.*, 1995).

Low pH values in a river affect aquatic life and impair recreational uses of water (DWAF, 1992). A change in pH from that normally encountered in unimpacted streams affects the biota (DWAF 1992). pH affects many chemical and biological processes in the water. For example, different organisms flourish within different ranges of pH.

Low pH can also allow toxic elements and compounds to become mobile and available for uptake by aquatic plants and animals.

In this study, an attempt was made to assess the levels of some water quality parameters pH, Eh, DO, TDS nitrate, sulphate, phosphate and some trace heavy metals in Mario Jose tannery effluent from kano industrial area, Kano metropolis, Kano state Nigeria. This was with a view to estimate the levels of water pollution in Kano, Nigeria.

### MATERIALS AND METHODS

Industrial effluents from Mario Jose tannery were monitored through regular weekly grab sample collections for eight weeks. Grab samples were collected thrice a week at specified periods during peak production periods of the industries understudied. Measurement points from the sampling sites have been designated PS, 1 and 4 m. Point PS was located at the point of immediate discharge of the effluent. Point 1m was a point located approximately 100 m after the effluent discharge point and 4 m was located about 400 m after the effluent discharge point. The sampling was on daily basis. The sampling points were chosen to evaluate the environmental impact on the rivers.

pH, redox potential Eh, dissolved oxygen DO, total dissolved solids TDS, temperature and heavy metals concentration. Standard methods were followed in determining the above variable (Rand *et al.*, 1979). Sample measurements were determined in triplicate. The effluent pH, Eh and temperature ( $^{\circ}\text{C}$ ) were measured using WTW pH-Electrode sen Tix 41. Dissolved oxygen was measured with Jenway Model 9070 waterproof DO<sub>2</sub> meter. All probes were calibrated prior to measurement with the appropriate traceable calibration solution in accordance with manufacturers instructions.

For lead, chromium, zinc, copper, cobalt and manganese determination, the effluent samples were digested as follows. One hundred cube centimeter of the sample were transferred into a beaker and 5 mL concentrated HNO<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sup>3</sup> with distilled water (Radojevic and Bashkin, 1999). Determination of heavy metals in the effluent samples was done using Atomic Absorption Spectrophotometer (AAS, Unicam 969) as described in the manufacturers instruction manual.

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 (Standard Methods 1976 and DWAf 1992).

Nitrate as N was determine by the cadmium metal method (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 Ve (Standard Methods, 1976; DWAf, 1992).

Data collected was subjected to analysis of variance using the general linear models. One way analysis of variance (ANOVA) ( $p < 0.05$ ) were used to access whether heavy metal and anion concentrations varied significantly between and within sampling points, probability less than 0.05 ( $p < 0.05$ ) were considered statistically significant. All statistical calculations were performed with SPSS 9.0 for Windows (Ozdamar, 1991).

## RESULTS AND DISCUSSION

Concentrations of heavy metals in Mario Jose Tannery from the months of September to October are showed in Table 1. The order of metal content mean concentration is Cr>Fe>Zn>Mn>Pb>Co>Cu. Thus the concentration of Cr ( $2.70 \pm 0.57$  to  $3.22 \pm 0.54$  mg L<sup>-1</sup>) and Fe ( $1.09 \pm 0.56$  to  $1.20 \pm 0.13$  mg L<sup>-1</sup>) were higher than those of other metals between the sampled points. The values of Cr and Fe were above the limits set by FEPA and WHO of 1.0 and 1.5 mg L<sup>-1</sup>, respectively. High values for chromium mentioned above is due to the fact that chromium are compound of tannery effluent emanating from the used of chromium salt (Bajza and Vreck, 2001). The relatively high concentrations of Fe obtained when compared to other metals might be due to its abundance in earth's crust and also due to the fact that machinery of the tannery are made from iron and steel, the discharge would pose a threat to the environment and affect fauna and flora in the aquatic environment.

The concentration of Zn, Mn, Pb, Co and Cu fell within the range set up by FEPA and WHO allowed for the discharge of effluent into river.

Heavy metals in industrial effluent showed an increase in concentration with distance from point source up to 400 m, these increases in values might be as a result of accumulation of these metals along the sampling points or as a result of discharge from other sources, since Kano is an industrial area. Results of analysis of variance (ANOVA) indicated that variations among points were statistically significant in all metals except Cu and Fe ( $p < 0.05$ ).

From Table 2, the order of anion mean concentration is SO<sub>4</sub><sup>2-</sup>>NO<sub>3</sub><sup>-</sup>>PO<sub>4</sub><sup>3-</sup>. Concentrations of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> were higher than phosphate within the sampled points. The high mean values of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> were above limits set by FEPA of 0.2 mg L<sup>-1</sup> sulphate and 20 mg L<sup>-1</sup> Nitrate for discharged of tannery effluent in to river (OECD, 1982).

Sulphate levels in all the effluents studied varied from  $214.5 \pm 2.71$  to  $318.3 \pm 5.89$  mg L<sup>-1</sup>. The high values for sulphates 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. 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 (Bosmc *et al.*, 2000).

Nitrate levels in all the effluents studied varied between  $39.4 \pm 2.39$  to  $83.3 \pm 4.42$  mg L<sup>-1</sup> within points. 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

Table 1: Concentration (mg L<sup>-1</sup>) of metals in industrial effluent from mario jose tannery (Challawa Industrial Area) kano metropolis between the periods of September-October 2005

CODE	Cu	Co	Zn	Mn	Pb	Fe	Cr
PS	0.11±0.05 <sup>a</sup>	0.13±0.04 <sup>a</sup>	0.47±0.04 <sup>a</sup>	0.25±0.02 <sup>a</sup>	0.21±0.01 <sup>a</sup>	1.20±0.13 <sup>a</sup>	2.70±0.57 <sup>a</sup>
1 m	0.13±0.06 <sup>a</sup>	0.19±0.07 <sup>b</sup>	0.51±0.05 <sup>b</sup>	0.28±0.02 <sup>b</sup>	0.26±0.02 <sup>b</sup>	1.09±0.56 <sup>a</sup>	3.22±0.54 <sup>b</sup>
4 m	0.18±0.06 <sup>a</sup>	0.21±0.06 <sup>c</sup>	0.55±0.01 <sup>c</sup>	0.31±0.02 <sup>c</sup>	0.28±0.02 <sup>c</sup>	1.61±0.41 <sup>b</sup>	3.12±0.69 <sup>b</sup>

The values given in the table above are mean of replicate values (n = 16). Within columns, means with different letter are statistically significant, p<0.05, PS: Point Source (point of immediate discharge, 1 m: 100 m (from point of discharge), 4 m: 400 m (from point of discharge)

Table 2: Concentration (mg L<sup>-1</sup>) of some anion in industrial effluent from mario jose tannery (Challawa Industrial Area) kano metropolis between the periods of September-October 2005

Code	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	Temperature
PS	318.3±5.89 <sup>a</sup>	83.3±4.42 <sup>a</sup>	6.39±0.52 <sup>a</sup>	30.44±1.32 <sup>a</sup>
1 m	260.9±3.42 <sup>b</sup>	61.3±5.88 <sup>b</sup>	3.73±0.85 <sup>b</sup>	28.38±0.72 <sup>b</sup>
4 m	214.5±2.71 <sup>c</sup>	39.4±2.39 <sup>c</sup>	2.78±0.64 <sup>c</sup>	26.88±1.03 <sup>c</sup>

The values given in the Table above are mean of replicate values (n = 16). Within columns, means with different letter are statistically significant, p<0.05. PS: Point Source (point of immediate discharge), 1 m: 100 m (from point of discharge), 4 m: 400 m (from point of discharge)

in proteinaceous material (from liming unhairly operation) (Bosmc *et al.*, 2000). National and international bodies regulate the nitrate content in industrial effluent. FEPA state a limit of 20 mg L<sup>-1</sup> and the South Africa quidline for effluent discharge (DWF, 1992) state limit of 6 mg L<sup>-1</sup> nitrate levels as a safe limit 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 (OECD, 1982).

Phosphate levels in all the effluent varied within 2.78±0.64 to 4.58±0.52 mg L<sup>-1</sup>. These values were lower than limits set by FEPA of 5 mg L<sup>-1</sup>.

Anions in the effluent studied showed a decrease in concentration with distance from point source up to 400 m, this decrease might be as a result of self-purification of this anion along the sampling point or absorption of these anions within the wall of the discharged channel. Another possibility may be due to denitrification. Results of analysis of variance (ANOVA) indicated that variations among points were statistically significant for all the anion (p<0.05).

From Table 2, the effluent temperature significantly differ and were above the maximum permissible limits of 30°C set by FEPA at point source. Firstly relatively small increase in temperature kills certain species of fish, leaving oxygen-demanding waste to decay. Secondly, high temperature raises the metabolic rate of surviving fish and microorganisms, leading to increased oxygen consumption and thirdly oxygen is less soluble at higher temperature (Khan and Khamal, 2001). High temperature outside the optimum range for a prolong period of time, causes organisms to undergo stress and die (USEPA, 1991; Chapman, 1997). Point 1 and 4 m significantly differ and were below the maximum permissible limit of 30°C set by FEPA. Results of analysis of variance (ANOVA and t-test) indicated that variations among points were statistically significant (p<0.05).

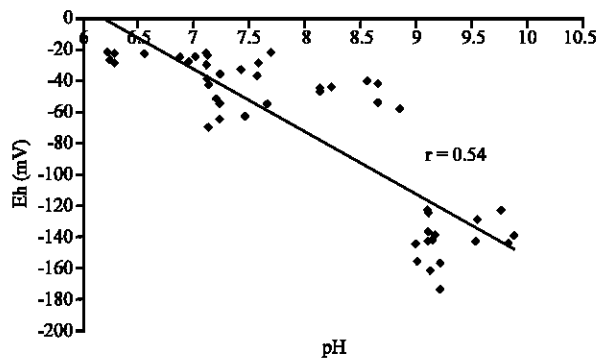


Fig. 1: Scatter plot of Eh and pH in industrial effluent from mario jose tannery, kano metropolis

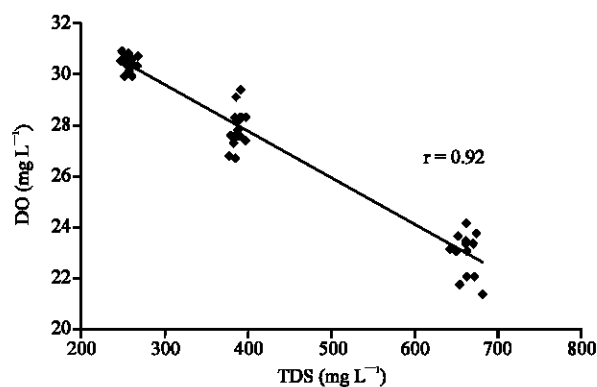


Fig. 2: Scatter Plot of DO vs TDS in industrial effluent from Mario Jose Tannery, Kano Metropolis

From Fig. 1, the pH values varied between 6.22 and 9.89 in the effluent and Eh values of -21 to -173 mv. Correlation analysis between Eh and pH values gives an inverse linear correlation. Negative values for Eh indicate that the environment is a reducing environment. The pH of most industrial effluent ranged between 6.5-9.0 (FEPA and WHO). The results obtained were within the acceptable levels (WHO). Of the sampling points; point source (PS) show higher pH values than point 1 and 4 m, which were alkaline. These high values might be as a result of the salts using for tanning.

From Fig. 2, The DO values varied between 21.4 to 30.7 mg L<sup>-1</sup> and TDS values of 246 to 681 mg L<sup>-1</sup>. A plot of DO and TDS gives an inverse linear correlation showing that as TDS increases in values DO decreases.

The TDS values were noted to be high at the point source (PS), corresponding to low DO values. The finding is in line with what (Ademoroti, 1996; Rand *et al.*, 1979; Symonds *et al.*, 1981) reported that a low DO usually depicts a high TDS values. The plot of DO against TDS values also emphasized this fact, with correlation of  $r = -0.92$ . From the Fig. 2 an increased in TDS correspond with a decrease in DO. Such occurrence might be possible due to the presence of high concentration of TDS and Turbidity from suspended solids which originate from all stage of leather making; they comprise fine leather particles, residues from various chemical discharges and reagents from different waste liquors. The above processes reduce water clarity, because cloudy water absorbs more heat and blocks light penetration, which prevent photosynthesis. Increased turbidity increases water temperature as suspended particles absorbed more heat; this in turn reduces the concentration of Dissolved Oxygen (DO) because warm water holds less Dissolved Oxygen than cold water. Dissolved Oxygen (DO) contents in all the sampled point were above the safety limits for maintenance of aquatic life of (5.00 mg L<sup>-1</sup>) Symonds *et al.*, 1981. The TDS concentration of all the sample points were within the limits set by FEPA and WHO of 2000 mg L<sup>-1</sup>.

### CONCLUSIONS

High concentrations of some trace metals (Cr, Fe,) have been observed to accumulate in Mario Jose tannery. These in addition to high levels of Dissolved Oxygen (DO), Sulphate and nitrate levels were above guideline values provided by FEPA and WHO, while pH, Eh and TDS levels in effluents were below guideline values.

Also heavy metals in industrial Effluent showed an increase in concentration with distance from point source up to 400 m while anions showed a decrease in concentration with distance from point source up to 400 m. Such elevated values for the above parameters measured are potential for profound effect on the water body itself and resident aquatic life. By extension it is also a potential for harmful effect on the residents of the area who depend on the river for life sustenance.

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