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Characterization of effluent discharge from tanneries in Challawa Industrial Estate, Kano, Nigeria using physicochemical-based indices

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Abstract
This study was conducted to characterize the effluent discharge of some tanneries in the Challawa Industrial Estate, Kano. Tannery operations consist of converting raw hide or skin to leather, which can be used in the manufacture of a wide range of products. Effluents were collected at the discharge point of each of the tanneries. Ex-situ analysis of the effluent samples for Total Suspended Solid (TSS), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Chromium, Cadmium, Chloride, Nitrate and Sulphide were determined using Standard Methods. Concentrations of Chromium ranges from 1.0mg/l to 2.4mg/l. The lowest value of 1.0mg/l was recorded in Mamuda Tannery and the highest value of 2.4mg/l in Fine Leather**.** Chloride ranges from 2415.5mg/l to 10929.9.Concentration of nitrate ranges from 591.2mg/l to 2814.0mg/l. the lowest value was recorded in Mamuda Tannery while the highest value was from Fine Leather. Cadmium concentration ranges from 0.006mg/l to 0.02mg/l, while Sulphide ranges from 54.7mg/l to 99.7mg/l. The concentrations of all ex-situ parameters except for Cadmium were higher than standard permissible limits (PL) set by the National Environmental Standards and Regulations Enforcement Agency (NESREA) for Textile, Wearing Apparels, Leather and Footwear Industries, Regulation 2009. These tanneries discharge their effluents into canals that eventually flow into the nearby Challawa River which is used for agricultural purposes by local farmers. Thus, the discharged tanning effluent in Challawa Industrial Estate, Kano pollutes the Challawa River. Based on the findings from this study, the following recommendations are made: Proper treatment of wastewater from the tanneries should be carried out to ensure all pollution parameters concentration are below the maximum permissible limits (PL) of regulating authorities before discharge; regulatory authorities need to embark on routine inspection and assessment of effluent treatment plants of tanneries to ensure proper treatment of effluents before it is discharged; secondary treatment plant should be installed in tanneries to treat primary effluents.

Keywords: Tanning; effluent; environment; heavy metals; pollution; characteristics.

Introduction

Tanning activities have been one of the most dominant occupations in Kano since the pre-industrial era. Tannery operations consist of converting raw hide or skin into leather, which can be used in the manufacture of a wide range of products such as shoes, bags, belts, seat covers, etc. (Assefa *et al*., 2000). While the olden days' tanners adopted the use of traditional and local method of tanning, industrialization brought about the use of synthetic chemicals in tanning processes. A variety of chemicals are used in the tanning process along with large quantities of water which are discharged as effluents. Chromium salts (particularly chromium sulphate) are the most widely used tanning substances to convert hide to leather (Aleem *et al*., 2003). Unfortunately only a fraction of the chromium salts used in the tanning process react with the skins. The rest of the salts remain in the tanning exhaust bath and are subsequently sent to a depuration plant where the chromium salts end up in the sludge. The wastewater generated which contains chromium salts is discharged into the environment (Aleem *et al*., 2003). In other words, not all the chemicals involved in the tanning process are utilized. Some traces of the utilized chemicals are channelled to the facility's Effluent Treatment Plants (ETPs). Besides, chemicals that are neither adsorbed nor rapidly lost by volatilization, are likely to be available for leaching, thereby contributing to pollution of groundwater

(Warren and Haack, 2001). Tanneries are heavy consumers of water and thus, a large volume of waste waters are released daily (Akan *et al*., 2009). Muhammad (2014) defined tannery effluent as undesirable waste material and substances which may be solids, liquids or gases that come out of the processes of leather manufacture. They are divided into solid, liquids and gaseous wastes. The liquid waste constitutes major pollutants to the environment.

The environment is under increasing pressure from the direct discharge of effluents from industries and municipal wastewaters into soils and water bodies. This has become a growing environmental problem (Wakawa *et al*., 2008). Nigeria at the moment is in a race to establish industries like tanneries, petroleum refineries, soaps and detergent, textiles and apparels, building materials and so on. All these industries produce various effluents that are discharged into the environment with most of the large cities in Nigeria feeling the pinch of pollution from industrial effluents (Mustapha, 2013). The tanning industry is recognized as a serious environmental threat all over the world (Wakawa *et al*., 2008). Isa and Jimoh (2013) ranked the tannery wastewater as the most polluting of all industrial wastewaters and thus, depending on the tannery process, wastewaters have varying characteristics depending on the pollution load.

In most developing countries voluminous tannery effluents are directly discharged to nearby open lands where they adversely affect the quality of both soil and groundwater, rendering them unsuitable for viable human use as well as the soil flora and fauna. These effluents contain toxic chemicals, including heavy toxic trace metals that turn tannery effluents into noxious wastewaters (Ates *et al*., 1997; Cooman *et al*., 2003). The groundwater is affected by the continued seepage of effluents (Wang *et al*., 1990), while the dissolved chemicals infiltrate into the surrounding soil, resulting in soil and water pollution, rendering the soil unfit for cultivation. Regulations put in place to protect the marine environment and other water bodies in Nigeria have not been effective in controlling the indiscriminate dumping of effluent into open water bodies (Akan *et al*., 2009). Most wastes and wastewaters from tanning industries are discharged into the environment without treatment (Akan *et al*., 2009). Tannery wastewater contains utilizable nutrients, but also toxic organic compounds that affect soil, surface and groundwaters, and thus, might pose a threat to the local communities. Several studies have indicated that tanneries in Nigeria, dispose of their waste indiscriminately into nearby water bodies (Mustapha, 2013).

The unregulated disposal of the chromium-containing effluent in both developing and developed countries has led to the contamination of soil, sediment, surface and groundwater, though, in trace amounts, chromium is considered an essential nutrient for numerous organisms, but at elevated levels, it is toxic and mutagenic (Wang *et al*., 1990). On a global scale, environmental pollution by industries via effluent discharge has become a threat to plants and animals and may ultimately threaten the quality of human life. World Health Organization [WHO] (2002) reported that discharged effluents from industries contain chemicals that are poisonous to humans and toxic to aquatic life. Gadd (1990) further stated that these effluents have a serious effect on plants, fish and animals, and are also a threat to human health. Effluents from industries can alter the physical, chemical and biological nature of receiving water bodies. Waste waters discharged into the environment without treatment could disturb the ecological balance (WHO, 2011).

Materials and Methods

The Study Area

Kano State is situated in the north western part of Nigeria, which is located approximately on latitude 11^0 59'N, longitude 8^0 34'E with an altitude of 486.5m. The state covers an area of 43,070 square kilometres. It borders to the north with Katsina State, west Kaduna State, to the south with Kaduna and Plateau States, while to the east, it bordered with Jigawa State. The state has a population of 9,383,682 people according to the National Population Commission, 2006. The climatic condition of the area is characterized by the dry and rainy season. The rainy season usually commences in April to September with the highest intensity usually in August. The dry season often lasts from October to April (Maconachie, 2007). ChallawaIndustrial Estate is located along Panshekara Road. It is bordered to the West by Zawachiki Town, to the East by Kumbotso Town, to the South by Yadanko Village and to the North by Panshekara Town (Maconachie, 2007).

Research Design: Data Collection

Primary data was obtained from laboratory analysis of effluent samples collected from the tanneries while secondary data was obtained from effluent limitation

standards for tanning and leather finishing provided by NESREA in the National Environmental (Leather, Wearing Apparel) Regulations, 2009.

Sampling Technique and Sample Size

Sampling was limited to four tanneries, viz; Fata Tannery, Mamuda Tannery, GB Tannery and Fine Leather tanneries. Three effluent samples labelled A, B and C were taken from each of the four tanneries at a weekly interval for four (4) weeks; after two to three trials, the average value of each parameter was determined and tabulated as outlined by NESREA training manual for laboratory technologists (2009).

Laboratory Analysis of Effluent Samples

The physico-chemical parameters for laboratory analyses selected were: Total Suspended Solid (TSS), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Sulphide, Nitrate, Chloride, Cadmium and Chromium of 100ml of three (3) samples of effluent collected at the discharge point of effluent treatment plant (ETP) of the four (4) tanneries before discharge from the tanneries at Challawa Industrial Estate Kano. A detailed analysis of the effluent samples was done by adopting the standard method for the Analysis of Water and Wastewater as described by NESREA Training Manual for Laboratory Technologists (2009) to determine the quality of water released by the tanneries. Furthermore, the date and time of sampling were recorded and laboratory condition was also noted when conducting the analysis. The methods adopted in the determination of each parameter are discussed below:

Data Analysis

Descriptive statistics were used in data analysis where mean concentrations of values were taken on all the parameters. SPSS version 21 was used for the analysis.

Results

Physicochemical characterization of effluent discharge from tanneries at Challawa Industrial Estate, Kano

The results of the effluent samples discharge from four tanneries at Challawa Industrial Estate, Kano are presented on Tables 1 to 5.

Table 1: Physicochemical parameters determined in the effluent discharge from four tanneries in Challawa Industrial Estate, Kano. Result from first week of study

					Facilities:	
S/No	Parameter (mg/l)	Fata Tannery	Fine Leather	Mamuda Tannery	GB Tannery	NESREA (PL)
1.	Total Suspended Solid	118	149	78	122	25
2.	Biological Oxygen Demand	70	120	110	115	50
3.	Chemical Oxygen Demand	210	312	180	381	160
4.	Cadmium	0.0058	0.03	0.0039	0.03	0.02
5.	Chromium	1.39	3.91	1.04	1.30	0.50
6.	Chloride	20500	36819.83	7200.02	12790.61	500
7.	Nitrate	696.77	8784.27	389.04	2489.41	10.0
8.	Sulphide	115.30	198.09	78.90	101.87	1.0

Sample A: Date of analysis 19/07/2019

Table 2: Physicochemical parameters determined in the effluent discharge from four tanneries in Challawa Industrial Estate, Kano. Result from second week of study

					Facilities:	
S/No	Parameter (mg/l)	Fata Tannery	Fine Leather	Mamuda Tannery	GB Tannery	NESREA (PL)
1.	Total Suspended Solid	120	134	111	119	25
2.	Biological Oxygen Demand	100	109	88	111	50
3.	Chemical Oxygen Demand	187	212	177	205	160
4.	Cadmium	0.01	0.03	0.0098	0.012	0.02
5.	Chromium	2.21	2.40	1.10	1.48	0.50
6.	Chloride	1800	2750	981	1278	500
7.	Nitrate	807	957	776	841	10.0
8.	Sulphide	44	79	56	77	1.0

Sample B: Date of analysis 31/07/2019

Table 3: Physicochemical parameters determined in the effluent discharge from four tanneries in Challawa Industrial Estate, Kano. Result from third week of study

					Facilities:	
S/No	Parameter (mg/l)	Fata Tannery	Fine Leather	Mamuda Tannery	GB Tannery	NESREA (PL)
1.	Total Suspended Solid	98	139	78	114	25
2.	Biological Oxygen Demand	105	113	87	95	50
3.	Chemical Oxygen Demand	251	266	144	158	160
4.	Cadmium	0.032	0.038	0.004	0.021	0.02
5.	Chromium	1.80	2.10	1.01	1.20	0.50
6.	Chloride	2422	2240	781	1148	500
7.	Nitrate	754	844	642	722	10.0
8.	Sulphide	73.90	68	42	68	1.0

Sample C: Date of analysis 09/08/2019

Table 4: Physicochemical parameters determined in the effluent discharge from four tanneries in Challawa Industrial Estate, Kano. Result from fourth week of study

					Facilities:	
S/No	Parameter (mg/l)	Fata Tannery	Fine Leather	Mamuda Tannery	GB Tannery	NESREA (PL)
1.	Total Suspended Solid	119	126	101	109	25
2.	Biological Oxygen Demand	102	114	86	103	50
3.	Chemical Oxygen Demand	198	206	121	132	160
4.	Cadmium	0.016	0.02	0.01	0.02	0.02
5.	Chromium	1.40	1.32	0.91	1.12	0.50
6.	Chloride	1886	1910	700	896	500
7.	Nitrate	198	671	558	585	10.0
8.	Sulphide	37	54	42	60	1.0

Sample D: Date of analysis 20/08/2019

Table 5: Mean concentrations (mg/l) of analyzed parameters from the four selected tanneries in the Challawa Industrial Estate, Kano

					Facilities:	
S/No	Parameter (mg/l)	Fata Tannery	Fine Leather	Mamuda Tannery	GB Tannery	NESREA (PL)
1.	Total Suspended Solid	113.7	137	92	116	25
2.	Biological Oxygen Demand	94.2	114	92.7	116	50
3.	Chemical Oxygen Demand	211.5	249	155.5	219	160
4.	Cadmium	0.01	0.02	0.006	0.02	0.02
5.	Chromium	1.70	2.40	1.0	1.2	0.50
6.	Chloride	6652	10929.9	2415.5	4028.1	500
7.	Nitrate	613.9	2814	591.2	1159.3	10.0
8.	Sulphide	67.5	99.7	54.7	76.7	1.0

Discussion

Effluent Discharge Characteristics

The laboratory analyses of effluent samples to determine their characteristics from the four tanneries are shown in Tables 1 to 4. The mean concentration of the values is shown in Table 5. These parameters showed a slight difference among the sampling sites (tanneries). The Total Suspended Solids were observed to be very high in all the tanneries sampled and thus exceed the standard permissible limit set by NESREA. The mean concentrations of Total Suspended Solid are 113.7mg/L in Fata tanning company, 137mg/L in Fine Leather, 92mg/L in Mamuda and GB Tannery has 116mg/L. A similar study conducted in Sharada Industrial Estate, Kano by Ogabiella *et al*. (2007) recorded a mean concentration of Total Suspended Solid of 391mg/L, 324.8mg/L and 291.6mg/L. The differences in values might be

attributed to the method of treatments, nature and concentrations of chemicals used. The values obtained from this study are higher than the maximum permissible standard of 25mg/L for TSS set by NESREA.

The Biological Oxygen Demand (BOD) of the analyzed effluents has mean values of 94.2mg/L in Fata, 114mg/L in Fine Leather, 92.7mg/L in Mamuda and 116mg/L in GB Tannery. The mean concentrations of Chemical Oxygen Demand (COD) shown in Table 5 have values of 211.5mg/L, 249mg/L, 155.5mg/L and 219mg/L for Fata, Fine Leather, Mamuda and GB Tanneries respectively. A previously reported work carried out in some selected sites in Challawa Industrial Estate, Kano by Lawal (2006) between January to March, 2005 showed BOD concentrations of 300mg/L, 252mg/L and 325mg/L and COD concentrations of 806mg/L, 728.9mg/L and 629.5mg/L. The disparity in values might be as a result of differences in time of study and poor treatment of wastewater especially during festive periods when supplies for hides and skins are high. The concentrations are generally very higher than the standards set by NESREA. The higher concentrations may be due to heavy organic and chemical load in the tanning wastewater as a result of poor treatment of influent. The values obtained for COD are relatively higher than that of the BOD indicating that the effluents are mostly polluted by non-oxygen dependent bacteria to the toxic water condition.

Cadmium is a very hazardous metal to man and other living organisms especially when present in the aqueous medium (Olowu *et al*., 2012). In this study, the highest mean concentrations (0.02mg/L) was observed in Fine Leather and GB Tannery (Table 5). In a study conducted by Koki and Jimoh, (2013) from Challawa Industrial Estate, Kano tannery wastes dumping site, the results showed the highest value of 0.014mg/L in tanning sludge sampled. It is interesting to note that the levels are below the allowable limit of 0.02mg/L set as the maximum concentration of Cadmium allowed in Nigeria in NESREA gazette regulation "National Environmental (Chemicals and Pharmaceuticals, Soaps and Detergents) Regulation 2009.

Chromium concentrations are high in all the sampling sites; the highest concentration was obtained in Fine Leather (2.4mg/L) and the lowest concentration at Mamuda Tannery (1.0mg/L).This report confirmed the work of Olowu *et al*. (2012) who reported Chromium concentrations of 1.6mg/L and 3.0mg/L. The values are above the established critical limit of 0.5mg/L in both land and water application set by NESREA. The variation in the level of Chromium concentrations among the tanneries may be related to the treatments carried out. This can be confirmed from the report of Akan *et al.* (2009) which stated the poor conditions of the primary treatment plants of the tanneries make it difficult for proper treatment. Thus, sludge and wastewater from these tanneries may be a source of Chromium contamination if deposited on soil, as the high concentration above normal range is highly unsafe and pose health risks to the environment.

Chlorides values also vary among the sampling sites with Fine Leather having the highest value of 10929.9mg/L and the lowest value recorded in Mamuda Tannery with 2415.5mg/L. All the values recorded exceed the critical limit of 500mg/L of NESREA regulation "National Environmental (Textile and Wearing Apparel, Leather and Footwear Industries) Regulation, 2009. The values recorded in this study confirmed a previous report by Lawal (2006) who recorded mean values (2632mg/L, 2450mg/L and 2787mg/L) exceeding the standard permissible limit of the Federal Ministry of Environment on the application of chlorides on land and in the water of 500mg/L. The exceeded values might be a result of large quantity of Sodium-chloride applied for the preservation of raw hides and skins before processing and of course due to poor functioning of the primary Effluent Treatment Plants.

Sulphide mean concentrations of 67.5mg/L, 99.7mg/L, 54.7mg/L and 76.7mg/L in Fata, Fine Leather, Mamuda and GB Tannery respectively exceed the critical limit of 1.0mg/L of NESREA regulation. The high concentrations of Sulphide in all the sampled industries might be attributed to the large quantity of the chemicals used in the removal of hairs from hides and skin in the tanning processes. The tanning processes of the tanneries can contribute to environmental pollution. The tanneries discharge their effluents into canals that eventually flow into the nearby Challawa River which is used for agricultural activities by local farmers.

Conclusion

This study revealed that the discharged effluents from the tanning industries in Challawa Industrial Estate,

Kano have concentrations of pollution parameters such as Chromium with the lowest value of 1.0 in Mamuda Tannery and highest of 2.4 in Fine Leather, Chloridewith 2415mg/l and 10929.9mg/l, Nitrate with 591.2mg/l and 2814.0mg/l and Sulphide with 54.7mg/l and 99.7mg/l respectivelyare higher than the maximum permissible limit set by the National Environmental Standards and Regulations Enforcement Agency (NESREA) in its gazette regulation on Textile, Wearing Apparel, Leather and Footwear Industries, 2009. This is a clear indication that regulations to protect the environment were not adhered to by the tanneries. Generally, effluents from the tanneries were discharged into the environment without proper treatment.

Recommendations

Based on the findings from this study, the following recommendations are made:

- Proper treatment of wastewater should be carried out in tanneries to ensure all pollution parameters concentration is below the maximum permissible limits of regulating authorities before discharge.
- Regulatory authorities need to embark on routine inspection and assessment of effluent treatment plants of tanneries to ensure proper treatment of effluents before it is discharged.
- Secondary treatment plants should be installed in tanneries to treat primary effluents.

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