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Organic Pollution Profile and Anions of Effluents from Challawa Industrial Layout and its Impact on the Water Quality of the Receiving River Challawa, Kano, Nigeria

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Abstract

Organic pollution profile and anions of effluent from Challawa industrial layout and the water quality status of the receiving challawa River were thoroughly assessed following standard analytical procedures. Results indicated that both effluent and surface water showed the ranges 8.72-8.89 and 7.23-7.65 for pH, 28.6-30.2 and 27.56-28.23 ^{o}C for temperature, 135.56 mg/l - 154.34mg/l and 48.8mg/l - 86.46mg/l for sulphide, 325.67-358.98 and 156.43-241.98 mg/l, for chloride, 262.62-287.84 mg/l and 87.93-113.52 mg/l for BOD and, 674.24-863.24 mg/l and 243.47-294.48 mg/l for COD. The mean effluent sulphide, BOD and COD concentrations were found to be above the Nigerian Environmental Standards and Regulations Enforcement Agency (NESREA) acceptable limits for the discharge into surface water. Chloride level was above WHO limits for discharge into surface water but below NESREA limits. The concentration of sulphide, BOD and COD in surface water were also found to be above World Health organization (WHO) and the Nigerian Standard for Drinking Water Quality (NSDWQ) acceptable limits for portable water. The study revealed that effluent discharged from Challawa industrial layout has significant adverse influence on the overall water quality of the receiving Challawa River. The need to enforce adequate effluent treatments before discharge into surface water is strongly advocated to reduce potential environmental hazards.

Keywords: Organic pollution; Anion; Effluent; Water quality; River Challawa.

1. Introduction

In most developed and developing countries, rapid industrialization and man's constant quest for comfort as well as change in taste and fashion has resulted to various forms of advancement in science and technology. [1]. One of the most critical problems faced by developing countries as a result of this rapid industrial growth is improper management of wastes generated by anthropogenic activities [2]. Industrialization is considered the bedrock of development strategies due to its significant contribution to economic growth and human welfare, but it carries with it, various devastating ecological and human disasters which have implicated industries as major contributors to environmental degradation and pollution problems of different magnitudes I [3]. Industrial waste water originates from the wet nature of industries which require large quantities of water for processing and disposal of wastes. Wastewater contains offensive and potentially dangerous substances which cause pollution and contamination of receiving water bodies [4]. Water bodies near industrial area have been extremely affected from disposal of waste which can alter their physical, chemical and biological nature. Wastewater constituents are classified as organic, inorganic, particulate and pathogenic. An increase in the concentration of dissolved or suspended organic materials stimulates the growth of bacteria. The organic matter concentration of effluent discharge can be so great that the receiving water body is completely devoid of oxygen [5]. An important pollution index of industrial wastewaters therefore is the oxygen function measured in terms of chemical oxygen demand (COD), and biological oxygen demand (BOD). Organic material is anything living or once living. Examples of organic wastes are dead plants and animals and sewage. BOD measures the amount of dissolved oxygen required by aerobic biological organisms in water to break down organic material present in it at certain temperature over a specific time period [6] and is a good gauge of stress to the stream ecosystem. BOD is used to quantitatively evaluate the organic load in a water body. Comparison of BOD and DO measurements indicates stresses to the stream. High BOD and low DO indicates a stress from pollutant loads, while low BOD and low DO indicates other stressors [7]. The total quantity of oxygen required for oxidation of all organic materials into carbon dioxide and water is measured using chemical oxygen demand (COD). COD does not differentiate between biologically available and inert organic matter [7]. The nutrient status of wastewater on the other hand is measured in terms of nitrogen and phosphorus [3]. The discharge of effluent containing high level of nutrients into a body of water often triggers serious water pollution problems as aquatic plants present in the water tend to grow and reproduce faster. Should algae grows in high density on the

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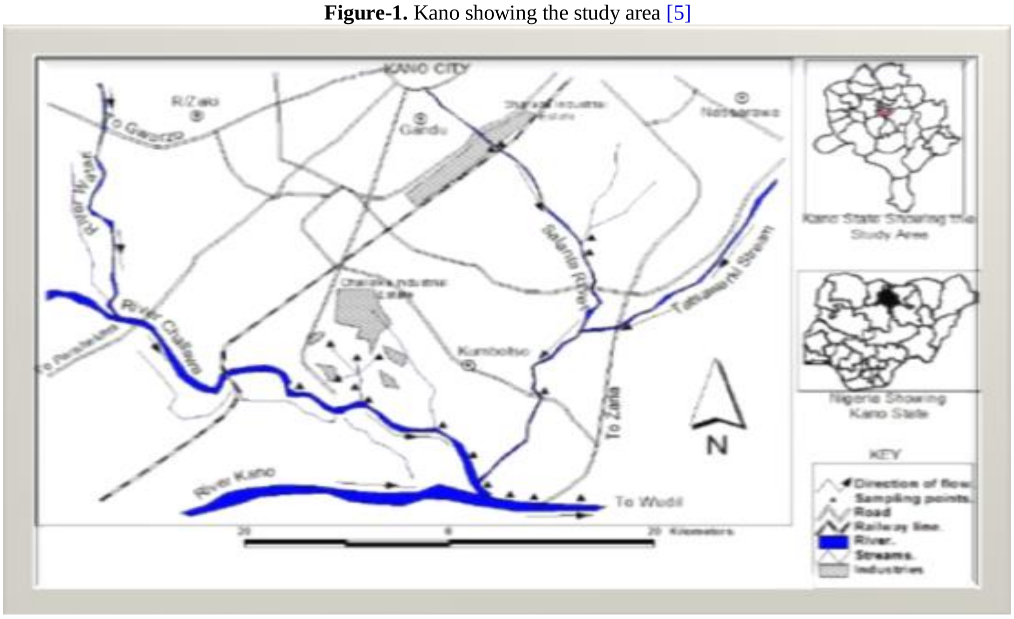
surface, sunlight is shaded from reaching plants at greater depths leading to the death of such benthic plants. When algae die, the decaying process uses oxygen in the water. Decreasing the amount of dissolved oxygen will cause aquatic animals to die. The process of aquatic overgrowth, followed by death, decay, and oxygen depletion is commonly referred to as eutrophication [8]. Eutrophication of water bodies, results in the destruction of fisheries and decrease in the aesthetic and recreational values of water resources [8, 9]. The indiscriminate discharge of effluents and municipal sewage into the river jeopardizes to a great extent the health of aquatic living organisms, introduces harmful bacteria, viruses and other pathogens that can spread diseases thus resulting in high risk to public health [10]. The major industries in Kano city include tanneries, textiles, chemicals and allied products. The city hosts over 70% of tannery in Nigeria. Most of the tanneries in are located in Challawa industrial area [11]. Tannery effluent is by- product of the manufacturing and transformation of hides and skin to leather products [12]. It is a major source of environmental degradation and pollution because of the huge volumes generated and discharged untreated or with minimal treatment due to cost implication. Tannery waste water is considered one of the most polluted industrial waste water. The level of environmental degradation arising from industrial discharges from canals and channels which eventually flows into Challawa River in Kano is alarming. River Challawa is an important resource which supplies water for irrigation, drinking water after treatment, agricultural and fishing activities. Sufficient environmental monitoring and planning is absolutely necessary to protect the environment from further de gradation and to safe guard public health. Kano is on record the most populous city in Nigeria. The devastating effect of an epidemic of water, or air borne disease in the city is better imagined, this study was therefore designed to assess the organic pollution profile and anions of industrial effluents and its impact on the water quality status of River Challawa. Implications of findings to public health are fully discussed

2. Materials and Method

2.1. Study Location

Kano (Lat. 11° 59 m 18.3s N, Long 08° 32 m 05.8s E) 418 m above sea level is located in Kano State, occupies central position of Northern Nigeria [13]. Industrially, it is one of the most developed cities in Northern Nigeria with three main industrial estates namely Bompai, Challawa and Sharada. Each harbours large number of wet industries tannery and textile are some of its dominating industries. The indiscriminate discharges of untreated effluent need to be addressed urgently. Presently the state is experiencing myrids of problems that are challenging its sustainable development [14, 15]. Effluent from Challawa industrial estate are discharged untreated through drains and canals that eventually flow into Chalawa River. Challawa River (Lat 11° 52 m 41s N, Long 08° 28 m 09s E) 515 m above sea level originate from the Challawa Gorge dam in Challawa village and stretches down to River Kano where it empties into Lake Chad [13]. The river receives waste from tanneries and textile industries, urban water storm and agricultural runoff from farming communities along the river course. The River is a major source of water supply to a large number of communities along its course. It is also used for irrigation, bathing, fishing, etc. The domestic water supply for Challawa, Sharada and Bompai industrial areas and the surrounding environment in general comes from River Challawa.

Figure-1. Kano showing the study area [5]



2.2. Sample Collection and Preservation

Procedure for sample collection preservation and preparation was adopted from American Public Health Association [16]. Three sampling points were established along the canal through which effluents from Challawa Industrial areas is channelled to River Challawa. The first point (Effluent station 1) was established at the confluence where the different drains converge. The second point (Effluent station 2) was 500 meters from Sampling station 1, the third point (Effluent station 3) was at the point just before the effluent is discharged into the River Challawa. Four sampling points were also established along Callawa River. The first point (River station 1) was at the point source (the identified effluent discharge point) and point number two (River station 2) was 500 meters downstream of sampling station 1 and the third point (River station 3) was 500 meters downstream of sampling station 2. The fourth point (River station 4) was 1000 meters upstream of the point source (Sampling station 1) serves as the control. A total of seven samples were collected monthly from February to April 2016 corresponding to the peak of the dry season. Effluent and water samples were collected by simple scooping using plastic bucket and poured into 2 litres plastic containers previously cleaned by washing with detergent, rinsed with clean water, then distilled water before soaking in 10% Nitric acid for 24 hours American Public Health Association [16]. Temperature were determined on site electronically using HACH conductivity/TDS meter (model 44600.00, USA) and Zeal–tech digital pH meter (model 03112, India) respectively. The samples were kept in cooler stock with ice block and transported to the Environmental Laboratory, National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria, at a temperature of < 4^{o}C for preparation and analysis.

2.3. Sample Preparation and Analysis

Biochemical oxygen demand (BOD) was determined according to standard Methods for the examination of water and waste water [16]. The dissolved oxygen content was determined before and after incubation. Sample incubation was for 5 days at 20^{0}C in BOD bottle and BOD_5 was calculated after the incubation period. Determination of chemical oxygen demand (COD) was carried out according to the method described by Ademoroti. COD was determined after oxidation of organic matter in strong tetraoxosulphate (VI) acid medium by $K_2Cr_2O_7$ at 148^{0}C, with back titration [17]. Chloride was determined using Morh's method, one hundred (100) milliliters of the waste water sample was measured into a 250ml conical flask and pH was adjusted to 8 with 1MNaOH. 1 ml of K_2CrO_4 indicator was then been added and titrated with $AgNO_3$ solution. A blank titration was carried out using distilled water. Chloride (mg/l) was calculated according to standard methods [16, 17]. Sulphide was determined using HACH DR 2400 spectrophotometer.

2.4. Analytical Quality Assurance

In order to ensure the accuracy and reliability of the results obtained, all the reagents used- HNO_3, $K_2Cr_2O_7$ and NaOH (Riedel-deHaen, Germany), HCl, $AgNO_3$ and K_2CrO_4 (Sigma Aldrich, Germany) and, HF and $HClO_4$ (British Drug House Chemicals Limited, England) were of analytical grade.

2.5. Statistical Analysis

Data collected was subjected to statistical test of significance using the Analysis of Variance (ANOVA) test to assess significant variation in concentrations of the organic pollution parameters and anions across the sampling locations. Probability less than 0.05 ($p < 0.05$) was considered to be statistically significant. Duncan multiple test and Donnette T was adopted for multiple comparison of parameters between sampling stations depending on whether the homogeneity test was greater than or less than 0.05. SPSS software 17.00 for windows was used for all statistical analysis.

3. Results

3.1. Physicochemical Characteristics of Effluent and Surface Water

Result obtained from the determination of physicochemical characteristics of both industrial effluents discharged from challawa industrial estate and surface water across the different sampling points along Challawa River, Kano around Challawa Industrial Area are presented in Table 1 while the spatial distribution of the Average concentration of physicochemical properties surface water across the different sampling points in the study area and the control are shown in Figures 2 and 3.

Table-1. Physicochemical parameters of tannery Effluents from Challawa Industrial Layout, Kano and the physicochemical properties of surface water along the Challawa River around the Industrial Area

Parameter	Sampling Month	Effluent Station 1	Effluent Station 2	Effluent Station 3	River Station 1	River Station 2	River Station 3	River Control
pH	February	8.84	8.79	8.76	7.43	7.32	7.23	7.12
	March.	8.89	8.87	8.73	7.54	7.51	7.43	7.12
	April	8.88	8.76	8.72	7.65	7.62	7.33	7.13
	Mean ± SD	8.87 ±0.03	8.81 ±0.06	8.74 ±0.02	7.54 ±0.11	7.48 ±0.15	7.33 ±0.10	7.12 ±0.01
	Range	8.72 -889			7.23 -7.65			
Temperature	February	29.8	29.4	28.6	27.97	27.85	27.56	31.11
	March.	30.2	30.1	28.8	28.22	28.23	28.02	31.21
	April	30.2	30.1	28.6	28.02	28.21	28.11	31.34
	Mean ± SD	30.07 ±0.23	29.87 ±0.40	28.67 ±0.12	28.07 ±1.83	28.07 ±1.86	27.90 ±1.82	31.22 ±0.64
	Range	28.6 -30.2			27.56 -28.23			
Sulphide	February	145.43	143.34	137.43	86.46	54.32	48.86	0.56

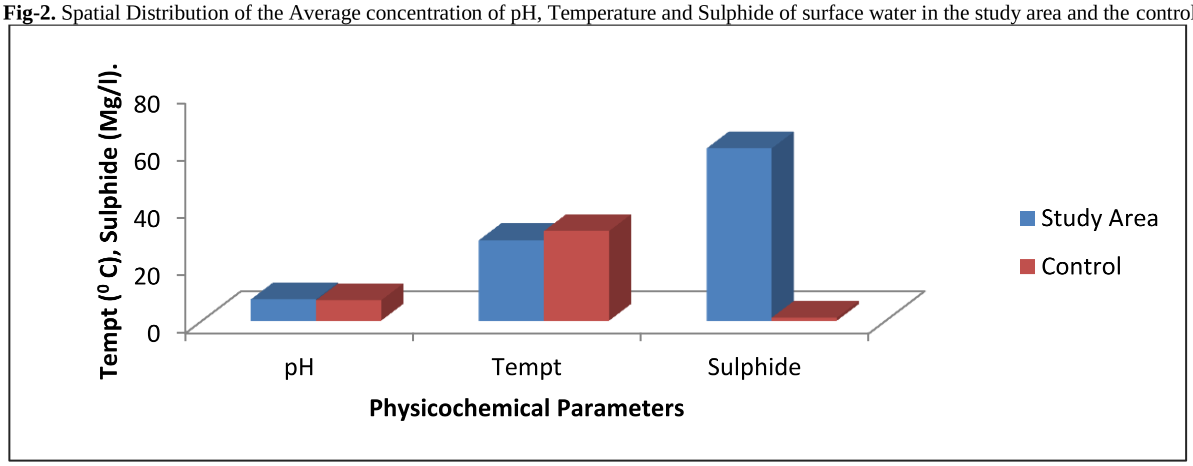
(mg/l)	March.	146.32	135.56	136.78	74.23	58.34	52.23	1.16
	April	154.34	145.56	136.65	54.87	56.64	54.39	1.45
	Mean ± SD	148.70 ±4.91	141.49 ±5.25	136.95 ±0.41	71.85 ±15.92	56.43 ±2.02	51.83 ±2.79	1.06 ±0.45
	Range	135.56 -154.34			48.86 -86.46			
Chloride (mg/l)	February	345.87	332.87	325.67	183.45	163.76	156.43	98.34
	March.	356.85	243.98	334.87	232.98	204.98	183.67	102.43
	April	358.98	346.43	336.91	241.98	221.65	203.62	107.99
	Mean ± SD	353.90 ±7.04	307.76 ±55.64	332.48 ±5.98	219.47 ±25.73	196.80 ±24.33	181.24 ±19.34	102.92 ±3.95
	Range	325.67 -358.98			156.43-241.98			
BOD (mg/l)	February	275.74	270.34	262.62	102.56	96.43	87.93	32.45
	March.	285.62	281.34	267.43	107.48	102.48	93.64	36.32
	April	287.84	276.43	262.53	113.52	104.61	97.32	38.83
	Mean ± SD	283.067 ±27.57	276.04 ±27.04	264.19 ±26.26	107.85 ±5.48	101.17 ±4.34	92.96 ±4.73	35.87 ±3.21
	Range	262.62 -287.84			87.93 -113.52			
COD (mg/l)	February	788.45	758.25	674.24	274.24	264.74	243.47	138.09
	March.	792.48	765.83	721.84	287.49	271.48	269.38	145.76
	April	863.24	772.13	73476	294.48	275.46	275.26	158.74
	Mean ± SD	814.72 ±34.34	765.40 ±5.67	24957.36 ±34.20	285.401 ±10.28	270.56 ±5.41	262.70 ±16.91	147.53 ±10.41
	Range	674.24 -863.24			243.47 -294.48			

Result obtained from the determination of physicochemical characteristics of industrial effluents discharged from challawa industrial estate and the physicochemical characteristics of surface water across the different sampling points along of Challawa River, Kano around Challawa Industrial Area (Table 1) indicates that the order of detection of pH of tannery effluent was; Effluent Station 1 > Effluent Station 2 > Effluent Station 3. Effluent pH values ranged between 8.72 and 8.89. The lowest pH value (8.72) was recorded at Sampling Station 3 in the month of April and the highest (8.89) at Effluent Station in March. The Effluent pH values were found to decrease gradually from the point of entry into the canal and were lowest at the point discharge into the River. Statistical analysis shows that the difference in effluent pH across the sampling stations was statistically significant (ANOVA, $p < 0.05$), station 1 being significantly higher than station 3. pH values of surface water across the sampling points displayed the trend River Station 1 > River Station 2 > River Station 3. pH values of surface water ranged from 7.23 in station 3 in the month of February to 7.65 in station 1 the month of April. The values were also found to decrease downstream. The difference in surface water pH across River stations was statistically significant (ANOVA, $p < 0.05$), with station 1 being higher than station 3. The average pH value of the control station (7.33±0.10) was found to be significantly (ANOVA, $p < 0.05$) lower than that of the established sampling points along Challawa River (Figure 2).

Table 1 shows that effluent temperature also followed the order: Effluent Station 1 > Effluent Station 2 > Effluent Station 3. Effluent temperature ranged between 28.6 and 30.2. The lowest temperature (28.6) was recorded at Effluent Station 3 in the month of February and the highest temperature (30.2) at Effluent Station 3 in March and April. The difference in temperature across the Effluent stations was found to be statistically significant at 95% confidence level. Effluent temperature at Effluent station 1 was significantly higher than Effluent station 3. Effluent station 2 was also significantly higher than Effluent station 3. The difference in temperature between Effluent station 1 and Effluent station 2 was not statistically significant (ANOVA, $p > 0.05$). Surface water temperature followed the trend River Station 1 > River Station 2 > River Station 3. Surface water temperature ranged from 27.56 at River station 3 in the month of March to 28.23 at River station 2 in the month of April. The difference in surface water temperature across the River stations was not statistically significant (ANOVA, $p < 0.05$). The average surface water temperature at the control station (27.90±1.82) was found to be significantly lower than that of the River stations under study (ANOVA, $p < 0.05$).

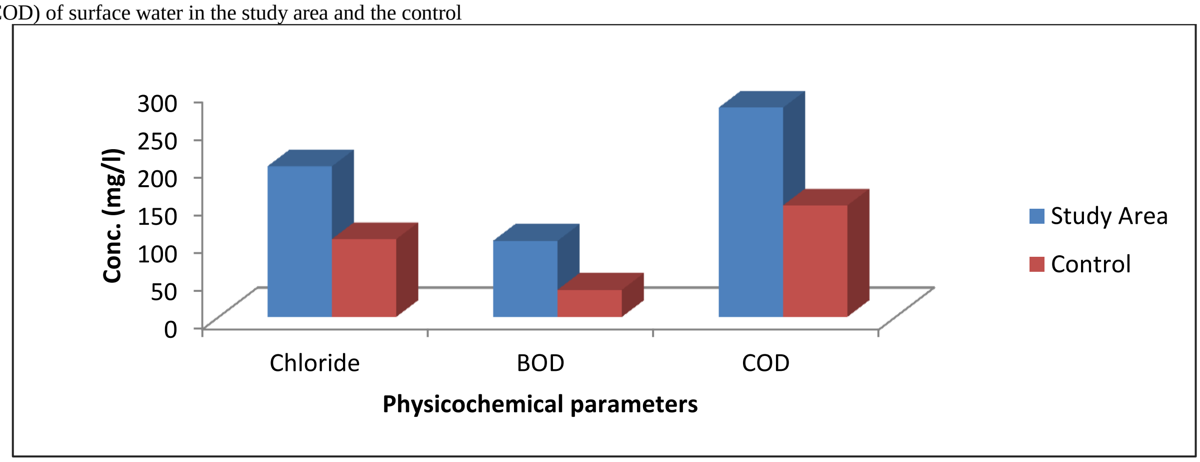
Sulphide in effluent was found to follow the sequence Effluent Station 1 > Effluent Station 2 > Effluent Station 3 (Table 1). The values ranged between 135.56 mg/l and 154.34mg/l. The lowest value was observed at effluent station 2 in the month of March while the highest value was observed at effluent station 1 in April. The difference in effluent sulphide across the sampling stations was found to be statistically significant (ANOVA, $p < 0.05$), Sulphide at effluent station 1 being significantly higher than effluent station 3. The difference in sulphide levels between effluent station 2 and effluent station 3 was not statistically significant at 95% confidence level. The sulphide levels at the difference sampling station along river challawa from the point source downstream followed the sequence: River Station 1 > River Station 2 > River Station 3. The range of values was between 48.8mg/l at river station 3 in February to at 86.46mg/l at river station 1 in same month. The difference in sulphide levels across the sampling stations along the river was not statistically significant (ANOVA, $p < 0.05$). However, the difference in average sulphide level between the sampling stations under study and the control was found to be statistically significant (ANOVA, $p < 0.05$), Sulphide levels at the control station (1.06±0.45mg/l) being significantly lower than the three established stations.

Fig-2. Spatial Distribution of the Average concentration of pH, Temperature and Sulphide of surface water in the study area and the control



The Average values of Chloride, Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) of industrial effluent across the effluent stations in the study also followed the sequence; Effluent Station 1 > Effluent Station 2 > Effluent Station 3. The ranges of the concentrations were: 325.67-358.98 mg/l for chloride, 262.62-287.84 mg/l, for BOD and 674.24-863.24 mg/l for COD. The minimum values for all three parameters (Chloride, BOD and COD) were recorded at effluent station 3 in the month of February and the maximum values at effluent station 1 in the month of April. Statistical analysis indicates that the differences in BOD and COD levels across the effluent stations were statistically significant (ANOVA, $p < 0.05$). The BOD of effluent samples at effluent station 1 was significantly higher than effluent station 3. Effluent station 2 was also higher than effluent station 3 at 95% confidence level but the difference between effluent station 1 and effluent station 2 was not statistically significant. The COD value at effluent station 1 was also found to be significantly higher than effluent station 3. The difference in COD between effluent station 1 and effluent station 2 and between effluent station 2 and effluent station 3 were not statistically significant. There was no statistically significant difference in Chloride levels across the effluent stations (ANOVA, $p > 0.05$).

Fig-3. Spatial Distribution of the Average concentration of Chloride, Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) of surface water in the study area and the control



The Average concentration of Chloride, Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) at the established river stations along River Challawa from the point source followed the trend: River Station 1 > River Station 2 > River Station 3. The concentrations ranged from 156.43-241.98 mg/l, 87.93-113.52 mg/l and 243.47-294.48 mg/l for chloride, BOD and COD respectively. The minimum values of the three parameters were recorded at River station 3 in the month of February and the maximum values at River station 1in the month of April. The average concentration of the parameters across river station 1, river station 2 and river station 3 were 219.47±25.73 mg/l, 196.80±24.33 mg/l and 181.24±19.34 mg/l for chloride, 107.85±5.48 mg/l, 101.17±4.34 mg/l and 92.96±4.73 mg/l for BOD, and 285.401±10.28 mg/l, 270.56±5.41 mg/l and 262.70±16.91 mg/l for COD respectively. The difference in BOD and COD across the River stations was found to be statistically significant (ANOVA, $p < 0.05$), River station 1 being significantly higher than River station 3 in both cases. The difference between River Station 2 and River station 3 were not significant for both parameters at 95% confidence level. There was no statistically significant difference in the chloride levels across the river station from the point source downstream through ought the study (ANOVA, $p > 0.05$). When compared, the average concentration of Chloride, BOD and COD at the established sampling stations from the point source (River station 1, 2 and 3) and the control

(Fig. 3) displayed statistically significant differences, the concentrations at the control station being significantly lower at 95% confidence level.

4. Discussion

Surface waters, both running as in rivers/streams (lotic ecosystems) and standing as in lakes/ponds (lentic ecosystems) are complex ecosystems with physicochemical and biological processes that interact with each other. A change of any one of those processes affects the delicate balance with the other processes and ultimately results in changes to the ecosystem. Organic pollution parameters and anions have been used to assess the surface water quality of Challawa River.

4.1. pH and Temperature

Mean pH values of effluent (Table 1) were fund to be within acceptable limits. The Nigerian Environmental Standards and Regulations Enforcement Agency's acceptable limit for the discharge of waste water to surface water and land application is between a pH of 6 – 9. A lower mean pH value of 7.56 was previously reported for major tanneries in Kano [18]. The mean pH of surface water in the study (Table 1) fell within the pH range (6.5-8.5) assigned by United State Environmental Protection Agency (US EPA), World Health organization (WHO) and the Nigerian Standard for Drinking Water Quality (NSDWQ) as standard pH for water, making it suitable for portability with respect to pH [19]. Mean pH values ranging from 7.21±0.02 to 10.46±0.01 have previously been reported for different sampling points along Challawa River (Wakawa *et al.*, 2008). A range of 7.45 - 8.63 have been reported for drains receiving water from tanneries in India [20], 7.1- 7.8

The average temperatures of effluents recorded in the study (Table 1) were found to be within the permissible limit. The maximum permissible limit set by the Nigerian Environmental Standards and Regulations Enforcement Agency (NESREA) for tanning and leather finishing industries stipulate that temperature must be less than 40 ^{0}C within 15 meters of out fall. The average surface water temperatures (Table 1) of the receiving Challawa River were found to be within the WHO standards of 30 ^{0}C – 35^{0}C for drinking water quality [21]. The significantly lower temperature recorded at the control station when compared to the other three river stations from the point source downstream suggest that effluent from tanneries around Challawa industrial area have significant influence on the quality of Challawa River. It also affects how much oxygen the water can hold. Cold water holds more oxygen. Increased water temperature lowers the amount of dissolved oxygen available for the aquatic life present and promotes excessive growth of aquatic plants and algae. Also, the toxicity of pollutants tends to intensify with an increase in temperature [22]. Temperature is therefore important to aquatic plants and animals and the overall health of the water [7, 19]. Surface Water temperature above 40 OC depicts polluted water [23]. The water temperature observed in this study is therefore within the permissible limit of water temperature for inland waters. A mean temperature of 28.5°C was reported for downstream area of River Galma while 25.7°C was recorded for upstream area of river Galma in 2011 [24]. A range of 18.6 - 30.3^{0}C have been reported for drains receiving waste water from tanneries in India [20].

4.2. Sulphide and Chlorides

The tanning industry is closely associated with the production of sulphide which emanates mostly in the liming yard and the anaerobic lagoons from the use of sodium sulphide and sodium hydrogen sulphide, and the breakdown of hair in the unhairing process [25]. The mean concentration of sulphide in effluents across the effluent stations (148.70±4.91 mg/l for effluent station 1, 141.49±5.25 mg/l for effluent station 2 and 136.95±0.41 mg/l for effluent station 3) as shown in Table 1 were above the effluent discharge standard (1mg/l) of the Nigerian Environmental Standards and Regulations Enforcement Agency (NESREA) for tanning and leather finishing industries. Under alkaline conditions, sulphides remain largely in solution. When the pH of the effluent drops below 9.5, hydrogen sulphide evolves from the effluent: the lower the pH, the higher the rate of evolution [26]. Effluent pH was found to be less than 9.5 at effluent station 1 and decreases steadily as it flows down. This could possibly be responsible for the decrease in sulphide level observed from effluent station 1 to effluent 3 and could thus account for the statistically significant difference in sulphide concentration between effluent station 1 and 3. Again Sulphides can be oxidized into non-toxic compounds by certain bacteria [26]. The continuous action of microorganism on the effluent may also contribute to the decrease in sulphide levels observed.

The mean sulphide concentration (71.85±15.92 for River station 1, 56.43±2.02 for River station 2 and 51.83±2.79 for River station 3) of surface water across the sampling stations along River challawa in the study (Table 1) were found to be above the Nigerian Standard for Drinking Water Quality (NSDWQ) permissible limit of 0.05 mg/l. Though the difference in sulphide concentration between the River stations was not statistically significant at 95% confidence level, the decrease in concentration observed downstream could be attributed to dilution as the contaminant flow downstream which is part of the self purification mechanism of flowing water bodies. Sulphide concentration at the control station (Fig. 2) was found to be significantly lower than the study area (River station 1, 2 and 3) indicating that effluent from challawa industrial estate has significant influence on the water quality of the River. The primary biochemical effects arising from H_2S exposure according to Nicholson, *et al.* [27] are, inhibition of the cytochrome oxidase and other oxidative enzymes, resulting in cellular hypoxia or anoxia. Concentration dependent toxicity occurs in humans following acute exposure. Exposure to moderate levels of H_2S (50–100 mg/l) can result in Keratoconjuntivitis, respiratory tract irritation and olfactory fatigue. Prolonged exposure to 250–500 mg/l will result in olfactory paralysis, severe lung and eye irritation, pulmonary oedema and unconsciousness in human [18, 28]. A mean sulphide concentration of 143.94 mg/l was reported for effluent from major tanneries in Kano [18].

Chloride in surface waters occurs naturally from the geology but high concentrations typically result from anthropogenic addition. Dissolved chloride is a good conservative element to use for quality assurance in a mass balance model because no natural biological or chemical processes remove or add chloride to the surface water. Therefore, the mass of dissolved chloride remains constant in the surface water unless there is a discharge to or withdrawal from the water body. The values of chloride across the effluent station under study were higher than the WHO standard of 150 mg/l for discharged into surface water but lower than the effluent discharge limit (600 mg/l) of the Nigerian Environmental Standards and Regulations Enforcement Agency (NESREA) for tanning and leather finishing industries. The high values of chloride in effluent is always attributed to the large quantities of hydrochloric acid, common salt (sodium chloride) and other chlorine containing compounds which are used as raw materials particularly in textile and tannery industries [29]. Being highly soluble and stable, they are unaffected by effluent treatment and nature, thus remaining as a burden on the environment [30]. This could be responsible for the fact that the difference in chloride levels observed across the effluent stations was not statistically significant. The use of effluents from challawa industrial area for the irrigation of crops therefore calls for serious concern. Ezike, *et al.* [18] had earlier reported a mean value of 235.72 mg/l for major tanneries in Kano. In their study of organic pollution indicators and anion concentrations of effluent and surface water in minna, Nigeria, Idris, *et al.* [3] reported higher mean values. 1767±29.53 mg/l was reported for the point of discharge of waste water in to the drain (S1), 1443±40.32 mg/l for 50m from S1 and 1314±28.22 mg/l for 100m from S1. Mean values of 642.50 ± 198.43 mg/l and 571.88 ± 131.69 mg/l respectively were reported for station I and station II at Unnao, uttar Pradesh, India for drains receiving effluents from tanneries [20].

The significant difference in chloride concentration observed between the control station and the river stations from the point source downstream (Fig. 3) indicates that chlorides discharged from challawa industrial area into River Challawa has a significant influence on the overall chloride concentration of the river. The decrease in chloride levels observed downstream could be due dilution or the natural self purification mechanism of the river. The chloride content or limit recommended by WHO and EPA is 250mg/l [10]. The chloride concentration recorded in the present study for River Challawa was therefore within the acceptable limits, the river under study therefore pose no toxicological risk with respect to chlorides concentration. Disruption of biological activities is a major concern of chlorides. Chlorides inhibit the growth of plants, bacteria and fish in surface waters; high levels can lead to breakdown in cell structure and can easily render aridity to exposed terrestrial ecosystems. [31, 32]. Chloride is almost completely absorbed in normal individuals, mostly from the proximal half of the small intestine. Intake of water containing sadium chloride above 2,5g/l over long period is reported to produce hypertension as well as 21% and 38% increase in the risk of contracting bladder and rectal cancer respectively [3]. Chloride concentration for the river under study was found to be similar to Shittu, *et al.* [21] who reported a range of 112mg/l-220mg/l for water used for drinking and swimming purposes in Abeokuta, Nigeria. Wakawa, *et al.* [29] reported mean chloride values ranging from 9.90±1.0 – 24.90±0.00 mg/l for River challawa in 2008. A mean value of 1591±23.03 mg/l was recorded for the point of discharge of waste water in to River Gorax (point source), 1330±27.07 mg/l for 200m down the river from the point source, 1204±30.25 mg/l for 400m downstream the point source and 1100±27.74 mg/l for 600m from the point source [3].

4.3. Biochemical Oxygen Demand and Chemical Oxygen Demand

The mean concentration of both effluents BOD and COD across the effluent station (Table 1) were far above the effluent discharge standard (50 mg/l and 160 mg/l respectively) of the Nigerian Environmental Standards and Regulations Enforcement Agency (NESREA) for tanning and leather finishing industries. The significant decrease in BOD and COD levels observed from effluent station 1 to effluent 3 and could be attributed to continuous action of micro organism as well as reaction between chemicals on the effluent as it flows down the canal.

The mean concentration of BOD and COD (Table 1) of surface water across the River stations along River challawa were found to be above acceptable standards. A measure of the quantity of oxygen used by microorganisms in the oxidation of organic matter if commonly referred to as Biochemical Oxygen Demand (BOD). BOD which is a very important water quality parameter that is used to evaluate organic pollution of surface water or pollution potential of effluent depends on; concentration of organic matter, extent of biological activities, temperature and other related factors. Ademoroti [17], defined BOD as the amount of oxygen required to break down into simpler substances the decomposable organic matter present in water and waste water at certain temperature and specified period. The mean values BOD across the river stations in this study were found to be far higher than the WHO allowable limit of 20 mg/l [33]. Desirable limit for BOD is 4.0 mg/l and permissible limit is 6.0 mg/l according to Indian standards. BOD demand below 3 mg/l is required for the best use of water [34]. The BOD values recorded in this study was found to be higher the 3mg/l required for best use of water as well as the permissible limit (6.0mg/l). Based on BOD classification of aquatic bodies, unpolluted (BOD < 1.0mg/l), moderately polluted (BOD 2-9mg/l) and heavily polluted (BOD > 10mg/l) [6, 35], River Challawa around Challawa industrial area may be designated heavily polluted by organic matter. Higher BOD values ranging from 1241 mg/l to 1654 mg/l for dry and wet season at the point source of River Challawa was previously reported by Adedokun and Agunwamba [5]. Lower values ranging from 10.00 mg/l to 70.00 mg/l were recorded for surface water of River Challawa [29]. Ubwa, *et al.* [36] reported a range between 9.00 and 861 mg/l for surface water around Gboko abattoir and a range of 0.92 mg/l – 786.7 mg/l was reported in Majawe, Nigeria [37]. A range of 1.85±0.04 to 3.47±1.32 (mg/l) has also been reported for surface water in minna Nigeria [3]. Discharge of effluent with a high oxygen demand directly into surface water, overloads the sensitive balance maintained in the water. Oxygen consumed in the decomposition process robs other aquatic organisms of the oxygen they need to survive. Organisms that are more tolerant of lower dissolved oxygen levels may replace a diversity of natural water creatures, which need oxygen (aerobic). The outcome is an environment populated by non-oxygen dependent (anaerobic) organisms leading to toxic water conditions. Dissolved oxygen depletion in water can encourage microbial reduction of nitrates to nitrites and sulphate to sulphide giving rise to odour problems. It can also cause increase in iron II concentration [6]. The presence of high BOD may indicate faecal contamination or increases in particulate and dissolved organic carbon from non-human and animal sources that can restrict water use and necessitate expensive treatment and impair ecosystem health. Increased concentrations of dissolved organic carbon can create problems in the production of safe drinking water if chlorination is used for disinfection, by-products such as trihalomethanes and other compounds toxic to humans, may be produced. It is, therefore, important to monitor organic pollution to identify areas posing a threat to health, to identify sources of contamination, to ensure adequate treatment, and provide information for decision making to enhance water sustainability [38]. The main limitation of BOD as an indicator of water quality is that it does not give an exact measure of the concentration of any particular contaminant. The five-day time frame to obtain results represents the main operational drawback of the indicator [38].

A measure of the amount of oxygen required for complete oxidation to carbon (IV) oxide and water of organic matter present in a sample of water, waste water (effluent) called chemical oxygen demand (COD) is another parameter used to assess the Oxygen demands of waste water [18]. COD does not differentiate between biologically available and inert organic matter. Since nearly all organic compounds are oxidized in the COD test, COD results are always higher than BOD results; this was confirmed in this study. Mean COD values of 91.31 ± 22.0 mg/l and 77.75 ± 10.38 mg/l respectively were reported for station I and station II at Unnao, uttar Pradesh, India for drains receiving effluents from tanneries [20]. These values were found to be lower than the effluent COD measured in this study. Higher Mean values ranging from 2389.00±133.50 mg/l to 3784.00±1234.00mg/l was recorded for effluent from tanneries and textiles in Kano [30].

Discharge of effluent with high oxygen demand into receiving surface water bodies' impact such water bodies adversely. Lower mean COD values ranging from 51.00±0.29 mg/l to 182.0±1.56 (mg/l) was reported for surface water in minna Nigeria [3]. Higher ranged from 170.00 mg/l – 570.00 mg/l [29] and 444 mg/l – 1508 mg/l [36] were reported for water used for drinking and swimming purposes in Abeokuta, Nigeria and for surface water around Gboko abattoir respectively. Lower mean COD values of 91.80mg/l and 40.80 mg/l were reported for River Onna and River Alareo in Ibadan Nigeria [39]. A range of 15.41 to 17 .28 was recorded for River Gumti in Uttar Pradesh [40]. The significant difference in both BOD and COD concentrations in the study between the control station and the established River stations from the point source downstream indicates that effluent from challawa industrial estate has significant influence on the water quality of the River. Chemical Oxygen Demand is an important water quality parameter which provides an index to assess the effect discharged wastewater will have on the receiving environment. Higher COD levels mean a greater amount of oxidizable organic material in the sample, which will reduce dissolved oxygen (DO) levels. A reduction in DO can lead to anaerobic conditions, which is deleterious to higher aquatic life forms. The COD test is often used as an alternate to BOD due to shorter length of testing time [41].

5. Conclusion

Despite the numerous environmental laws enacted to protect the environment, environmental degradation has continued unabated. Enforcement of environmental regulations is still poor as industries continue to discharge untreated/poorly treated waste water into the environment. The findings of this study revealed that effluent from Challawa industrial area has significant adverse influence on the water quality of the receiving Challawa River. Effluent sulphide, BOD and COD concentrations were found to be above the Nigerian Environmental Standards and Regulations Enforcement Agency (NESREA) acceptable limits for the discharge into surface water. Chloride level was above WHO limits for discharge into surface water but below NESREA limits. The concentration of sulphide, BOD and COD in surface water were also found to be above World Health organization (WHO) and the Nigerian Standard for Drinking Water Quality (NSDWQ) acceptable limits for portable water. It was concluded that, the number of environmental laws and regulations should not necessarily be seen as a yard stick for measuring their effectiveness because in the absence of the will to enforce such laws, they become useless. This study recommends that NESREA and other relevant authorities set up a more efficient control and enforcement mechanism to apply the existing legal provisions to safeguard the environment from further degradation.

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