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Organic Pollution Indicator And Anion Concentration Of Pharmaceutical Effluent And Surface Water In Minna, Niger State, Nigeria

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ABSTRACT
Pharmaceutical effluent and surface water from River Gorax Maitumbi industrial layout Minna, Niger State, Nigeria were Sampled at eight different points designated as S_1 to S_8. The levels of Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) were simultaneously monitored in the effluent and the receiving watersheds over a period of 3 months using standard method of APHA, (1995). Anion concentrations which includes phosphate (PO_4^{3-}), Nitate (NO_3^-) and Chloride (Cl^-) were also determined using standard procedures as discribed by HACH, (1997) and Ademoroti, (1996). Dissolved Oxygen value ranged from (3.67±0.20 to 7.00±0.22 mg/l); while COD showed the highest value of (182±1.56 mg/l) at S7 whereas BOD which range from (1.85±0.04 to 3.47±1.32 mg/l) was within permissible limits of 30mg/l. Similarly, anion concentrations showed values of 1.29 mg/l, 15.80 mg/l and 1767 mg/l to be highest at S1 for phosphate, nitrate and chloride whereas the lowest values of 0.69 mg/l, 7.21 mg/l and 950 mg/l were observed at the control (S5). Most values observed at ddifferent sampling points were outside the compliance levels of the NSDWQ, FEPA and WHO tolerance limits for effluents discharge into receiving watersheds except for PO_4^{3-} (1.29 ± 0.30 to 0.69 ± 0.05 mg/l) which was within permissible limits of 5mg/l. This study reveals the need for enforcing adequate effluent treatment methods before their discharge to surface water to reduce their potential environmental hazards.

***KEY WORDS**: Pollution, Environment, Watershad, Minna, River, Industry, Ions, Surface.*

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I. INTRODUCTION

An important pollution index of industrial wastewaters is the oxygen function measured in terms of chemical oxygen demand (COD), and biological oxygen demand (BOD), while the nutrient status of wastewater are measured in terms of nitrogen and phosphorus. In addition, other important quality parameters include pH, temperature and total suspended solids (Ezenobi, 2004). Pharmaceutical effluents are waste generated by pharmaceutical industry during the process of drugs manufacturing which is a serious contaminant. Thus the effluents from industries are considered as a serious environmental threat throughout the world (Wequar and Rajiv, 2009). Generally, pharmaceutical industries do not generate uniform waste streams, due to the variety of medicines produced during any given processing period (Houk, 1992). In recent times, a wide range of pharmaceuticals have been found in fresh and marine waters, and it has been shown that even in reduced quantities, some of these compounds are potentially capable of causing harm to both aquatic and terrestrial life forms (Jonathan and Nicolaos, 2005). Pharmaceutical and personal care products industries suffer from inadequate effluent treatment due to the presence of recalcitrant substances. Some of the most representative pharmaceutical and personal care products found in receiving waters include antibiotics, lipid regulators, antiinflammatories, antiepileptics, tranquilizers, and cosmetic ingredients containing oil and grease (Lateef, 2004). For example, characterization of the composite wastewater from soap, pharmaceuticals and food processing plants indicated that the waste was highly contaminated with organic compounds as indicated by COD and BOD values (Ekhaise and Anyansi, 2005).

The world global growth and rapid industrial development have led to the recognition and increasing understanding of interrelationship between pollution, public health and environment. Presently, some 2.4 billion people lack adequate sanitation and 3.4 million die each year in the world from water related diseases (Anonymous, 2001). In most developing countries like Nigeria, most industries dispose their effluents without treatment. These industrial effluents have a hazard effect on water quality, habitat quality, and complex effects on flowing waters (Ethan *et al*., 2003). Industrial wastes and emission contain toxic and hazardous substances, most of which are detrimental to human health (Jimena *et al*., 2008), (Rajaram, and Ashutost, 2008).

In Nigeria, main contributors to the surface and ground water pollution are the byproducts of various industries such as textile, metal, dying chemicals, fertilizers, pesticides, cement, petrochemical, energy and power, leather, sugar processing, construction, steel, engineering, food processing, mining and others. The discharge of industrial effluents, municipal sewage, farm and urban wastes carried by drains and canals to rivers worsen and broadens water pollution (Aziz *et al*., 2008). Effluents are dumped into various water bodies causing surface/ground water pollution and endangering biodiversity and lowering agriculture production. Study of rivers around industrial areas indicated that surface water resources are highly vulnerable to pollution as the entire stretch in the surrounding is heavily polluted with sewage and uncontrolled application of chemicals, so their effect on surface and ground water is an emerging concern (Rajan and Arias, 2007). Since many effluents are not treated properly, these products are discharged on the ground or in the water bodies (Odiete, 1999), and most of these discharges to water bodies accumulate in the system through food chain (Odiete, 1999).

Health effects of the consumption of pharmaceutical active compounds at low concentration levels are not fully understood (Kimura *et al.,* 2004). The levels of pharmaceutical active compounds found in drinking water pose a human health risk (Richardson, 2003). It has long been known that drugs are not wholly absorbed or broken down by the human body, significant amounts of any medication taken eventually pass out of the body, primarily through the urine (Kolpin, *at el*., 2002). Despite years of prodding by environmental scientists, the EPA has given very little attention to the dangers posed by widespread pharmaceutical contamination (Frick, 2001). According to a U.S. Geological Survey (USGS) study conducted back in 2002, antidepressants, blood pressure and diabetes medications, anticonvulsants, oral contraceptives, hormone replacement therapy drugs, chemotherapy drugs, antibiotics, heart medications and even codeine are all showing up in the water supplies of American cities. This study was the first national-scale evaluation of pharmaceutical drug contamination in streams, and roughly 80 percent of the streams tested were found to be contaminated as well (Frick, 2001).

Although industrialization is inevitable, various devastating ecological and human disasters which have continuously occurred over the last four decades, implicate industries as major contributors to environmental degradation and pollution problems of various magnitude (Abdel-Shafy and Abdel-Basir, 1991; Velagaleti and Burns, 2006).A report showed that people drinking chlorinated water over long periods have a 21% increase in the risk of contracting bladder cancer and a 38% increase in the risk of rectal cancer (Wesson, 1996; Howard, 2007). The study estimates that about 9 percent of all bladder cancer and 18 percent of all rectal cancer cases are associated with long-term consumption of chlorinated by-products. This amounts to over 20,000 new cases each year (WHO, 1999). Nitrates and nitrites may themselves be carcinogens or may be converted in the body to a class of compounds known as the nitrosamines, compounds that are known to be carcinogens (Howard, 2007). Excessive concentrations of nitrate in lakes and streams greater than about 5 milligrams per liter (measured as nitrogen), depending on the water body, can cause excessive growth of algae and other plants, leading to accelerated eutrophication or "aging" of lakes, and occasional loss of dissolved oxygen (Knepp and Arkin, 2006). The EPA standard of 10 milligrams per liter (measured as nitrogen). The U.S. Public Health Service has established 10 mg/L of nitrate-nitrogen as the maximum contamination level allowed in public drinking water. Nitrate-nitrogen levels below 90 mg/L and nitrite levels below 0.5 mg/L seem to have no effect on warm-water fish, but salmon and other cold-water fish are more sensitive (USGS, 2002).

II. MATERIALS AND METHODS

2.1.Sampling Area

Samples were collected from pharmaceutical company in Miatumbi industrial layout Minna and surface water from River Gorax which is about 160meters from the industrial site. River Gorax is geographical located between latitude 9^0 31^0 N and longitude 7^0 0^0 E in Chanchaga, Minna. Wastewater and surface water Samples were collected from Miatumbi industrial layout and River Gorax in Minna, the samples were collected in cleaned, dry polyethylene bottles which have been previously washed with 20% nitric acid and subsequently with demineralized water. The samples were collected from eight points designated as S_1 to S_8, point S_1 was at the point of discharge of waste water in to the drain, S_2 was 50 meters from point S_1, S_3 was 100 meters from point S_1, and S_4 was the point of discharge of waste water in to River Gorax. S_5 was 100 meters up the river away from the point of discharge in to the river to serve as control. Point S_6 was the sample collected 200 meters down the river from point S_4 which is the point of discharge in to the River; S_7 was 400 meters from point S_4, while point S_8 was 600 meters from point S_4. Samples collected were taken to the laboratory and were refrigerated at 4^oC prior to analysis. Sampling and analysis of each parameter was conducted for three months from September to November 2012.

2.2.Laboratory analysis

Dissolved oxygen was measured using DO-Meter which was calibrated prior to measurement with solution of 5%HCl in accordance with the manufacturer's instruction. Determination of chemical oxygen demand was carried out according to the method described by Ademoroti (1996). The COD of the water sample was calculated from the following expression.

COD (mg/l) = (V_b –V_s) x M x 16000 ml of sample

Where V_b = Volume of FAS for Blank

Vs = Volume of FAS for sample

M = Morality of FAS

The BOD_5 was computed by subtracting the DO after five days incubation from the DO measured on collection of samples at point in mg/l (BOD_5 =DO_i –DO_f). The concentration of Phosphate and Nitrate in the samples were determined using DR/2010 HACH Spectrophotometer, as discribed by HACH, (1997). Whereas, the Chloride (Cl^-) determination was carried out according to the method described by Ademoroti (1996). New standards were perpared for each parameter during every measuring month.

2.3.Statistical analysis

The data obtained were subjected to descriptive statistical analysis (95 % confident limit) using SPSS 9.0 The general linearized model (GLM) of SPSS was used to generate analysis of variance (ANOVA), means, standard error and range. Turkey multiple range test (TMRT) was used to test differences among all possible pairs of treatments. Correlation was performed using MS-Excel.

III. RESULTS AND DISCUSSION

Dissolved oxygen is a measure of the degree of pollution by organic matter, the destruction of organic substances as well as the self purification capacity which is a major indicator of water quality (WHO, 2000). The survival of aquatic life depends on a sufficient level of oxygen dissolved in water. Low dissolved oxygen (DO) primarily results from excessive algae growth which may be as a result of increased phosphorus and nitrogen concentration and high temperature (Kingston and Jassie, 1986). This may result in insufficient amounts of dissolved oxygen available for fish and other aquatic life. Table 1: showed average Dissolved Oxygen (DO) which ranged from 3.67±0.20 to 7.00±0.22 (mg/l), the dissolved oxygen observed in the drain was below required standard for sustaining aquatic life which is stipulated at 5mg/l, a concentration below this value adversely affects aquatic biological life, while concentration below 2mg/l may lead to death for most fishes (Chapman, 1997). Low concentrations of dissolved oxygen, when combined with the presence of toxic substances may lead to stress responses in aquatic ecosystems because the toxicity of certain elements, such as zinc, lead and copper, is increased by low concentrations of dissolved oxygen (Goyer and Clarkson, 2001).

Biochemical oxygen demand (BOD) is the amount of dissolved oxygen needed by aerobic biological organisms in water to break down organic material present in water sample at certain temperature over a specific time period. BOD is an effective indicator of organic quality of water and wastewater treatment plants (Clair *et al*., 2003). The average Biochemical Oxygen Demand (BOD) ranged from 1.85±0.04 to 3.47±1.32 (mg/l). BOD value was observed to be highest at S_6 with value of 3.47 ± 1.32 mg/l as compared to the control at S_5 with the lowest value of 1.85 ± 0.04 mg/l as showed in Table 1: Statistical analysis using ANOVA showed that there was significant difference between the eight sampling points. BOD also measures the biodegradable materials in water and helps in the development of bacteria and other organic byproducts (Manahan, 1994). The addition of sewage sludge to a coarse textured sandy and calcareous soils was reported to have improve the water holding capacity, cation exchange capacity, increase the availability of N, P, K, Cu, Zn, Fe, Mn, Na but with reduced biochemical oxygen demand (BOD) (Badawy and EI-Moitaium, 2001). From the mean results obtained it can be said that the industrial effluents have no much effect on the river water, since the observed values are below the WHO maximum standard value of 50 mg/l for discharge of wastewater into stream. From the mean values observed it can be suggested that water samples from River Gorax were not too far from the safe limits compared with WHO and FEPA standards.

Chemical Oxygen demand (COD) is the amount of oxygen required by organic matter for its oxidation by strong COD substance in water (Clair *et al*., 2003). The COD measures pollution of domestic and industrial waste, the waste is measure in terms of equality of oxygen required for oxidation of organic matter to produce CO_2 and water. In this study the average value of COD was 129.3 mg/l which is below the WHO set limit of 2003. The Chemical Oxygen Demand (COD) values ranged from 51.00±0.29 to 182.0±1.56 (mg/l). COD value was observed to be highest at S_7 with value of 182.0 ± 1.56 mg/l as compared to the control at S_1 with the lowest value of 51.0 ± 0.29 mg/l. It can also be said that the industries in question may not be the basic cause of contamination in to the River but a contributing factor since point S_6 to S_8 which is 600meters away from S_4

showed a mean values which are higher than the control and the point of discharge in to River Gorax at S_4 with 126.00 ± 5.60 mg/l as showed in Table 1.Nitrates (NO_3^-) and nitrites may themselves be carcinogens or may be converted in the body to a class of compounds known as the nitrosamines, compounds that are known to be carcinogens (Howard, 2007). The average value of nitrates in effluent was 2.25 mg/l. Excessive concentrations of nitrate in lakes and streams greater than about 5 milligrams per liter (measured as nitrogen), depending on the water body, can cause excessive growth of algae and other plants, leading to accelerated eutrophication or "aging" of lakes, and occasional loss of dissolved oxygen (Knepp and Arkin, 2006). Table 2: showed that the values of Nitrate (NO_3^-) concentrations range from 8.81±1.66 to 15.80±0.67 (mg/l), nitrate value was observed to be highest at S_1 with value of 15.8 ± 0.67 mg/l as compared to the control at S_5 with the lowest value of 8.81 ± 1.66 mg/l. Nitrate concentrations at all the sampling points were above WHO and FEPA standard of 5mg/l discharged of wastewater into stream. The Nigerian Standard for Drinking Water Quality reported that nitrate concentration above standard limits causes Cyanosis, and Asphyxia ('blue-baby syndrome") in infants under three months syndrome (NSDWQ, 2007).

The addition of phosphates to rivers through the activities of humans such as pharmaceutical and other industrial effluents can accelerate the eutrophication process of nutrient enrichment that results in accelerated ecological aging of lakes and streams (Murphy and Riley, 2001). Critical levels of phosphorus in water above which eutrophication is likely to be triggered, are approximately 0.03 mg/l of dissolved phosphorus and 0.1 mg/l of total phosphorus (SMEWW, 1996). The Phosphate (PO_4^{3-}) concentrations ranged from 0.69±0.05 to 1.29±0.30 (mg/l). Highest concentration of phosphate was observed in point S_1 with mean concentration of 1.29 ± 0.30mg/l as compared to the control at S_5 with mean concentration of 0.69 ± 0.05 mg/l as showed in Table 2: Therefore, it can also be said that the industries in question contributes significantly in contaminating the river since point S_6 which is 200meters away showed a means value of 1.03 ± 0.14 mg/l which is higher than the control and is comparable to concentrations of discharge in the drain. The discharge of raw or treated wastewater, agricultural drainage, or certain industrial wastes that contain phosphates to a surface water body may result in a highly eutrophic state, in which the growth of photosynthetic aquatic micro- and macro organisms are stimulated to nuisance levels.

The mean concentrations of chloride (Cl^-) in the wastewater channel ranged from 950±19.03 to 1767±29.53 (mg/l), the mean chloride concentration is high in all the sampled points, with S_1 having the highest concentration of 1443 ± 40.32 mg/l and the control which is 100 meters up the stream have the least concentration of 950±19.03 This show that the industrial effluent is responsible for surface water contamination above WHO, FEPA and NSDWQ permissible limits of 250 mg/l chloride concentration in river water. Drinking of chlorinated water over long periods have a 21% increase in the risk of contracting bladder cancer and a 38% increase in the risk of rectal cancer (Wesson, 1996; Howard, 2007). This amounts to over 20,000 new cases each year (WHO, 1999). Chloride is almost completely absorbed in normal individuals, mostly from the proximal half of the small intestine. Although, excessive intake of drinking-water containing sodium chloride at concentrations above 2.5 g/litre has been reported to produce hypertension (Christensen, 2000) this effect is believed to be related to the sodium ion concentration. The results for elemental concentration in wastewater and surface water samples from River Gorax showed highest mean concentrations at point S_1 for all the metals tested. This can be attributed to the fact that there were high anthropogenic activities at this point as compared to other points. Table 2: show the varying concentration of metals analysed at different sampling points, which was observed to decrease from S_1 to S_4 in the drain and from S_6 to S_8 down the stream, the mean concentrations were observed to be above the control at points S_5 for all the metals. Some trace metals are potentially toxic because they act on the cell membrane or interfere with cytoplasmic or nuclear functions after entry into the cell. Hence, their accumulation in the human body could result to malfunctioning of organs (Jarup, 2003).

Table 1: Mean Concentration of Dissolved Oxygen, Biochemical Oxygen Demand and Chemical Oxygen Demand in Pharmaceutical wastewater and surface water samples from River Gorax, Maitumbi industrial layout, Minna, Niger State, Nigeria

Parameters / Sample points	Concentrations (mg/l) DO	COD	BOD_5
S1	4.47 ± 0.26	51.00 ± 0.29	2.11 ± 0.18
S2	3.67 ± 0.20	63.00 ± 2.22	2.14 ± 0.03
S3	3.98 ± 0.18	79.00 ± 4.32	1.63 ± 1.32
S4	7.00 ± 0.22	126.0 ± 5.60	2.24 ± 0.64
S5	4.09 ± 0.62	82.00 ± 0.93	1.85 ± 0.04
S6	6.03 ± 0.18	165.0 ± 2.32	3.47 ± 1.32
S7	5.37 ± 0.09	182.0 ± 1.56	2.76 ± 0.34
S8	4.66 ± 0.24	160.0 ± 3.02	2.06 ± 0.18

All the mean are statistically significant at $p<0.05$

S_1 = point of discharge of waste water in to the drain, S_2 = 50m from point S_1, S_3 = 100m from S_1, and S_4 = the point of discharge of waste water in to River Gorax. S_5 = control 100m up the river. S_6 = 200m down the river from S_4, S_7 = 400m from S_4, S_8 = 600m from S_4.

able 2: Mean Concentration of Anions in Pharmaceutical wastewater and surface water samples from River Gorax, Maitumbi industrial layout, Minna, Niger State, Nigeria

Parameters / Sample points	Concentrations (mg/l) PO_4^{3-}	NO_3^-	Cl^-
S1	$1.29^a \pm 0.30$	$15.80^a \pm 0.67$	$1767^b \pm 29.53$
S2	$1.19^a \pm 0.31$	$13.50^b \pm 1.56$	$1443^a \pm 40.32$
S3	$1.03^b \pm 0.22$	$7.21^c \pm 1.80$	$1314^a \pm 28.22$
S4	$0.80^a \pm 0.13$	$9.84^a \pm 0.88$	$1591^a \pm 23.03$
S5	$0.69^a \pm 0.05$	$8.81^d \pm 1.66$	$950^a \pm 19.03$
S6	$1.03^c \pm 0.14$	$13.21^a \pm 2.40$	$1330^a \pm 27.07$
S7	$0.83^a \pm 0.12$	$11.74^e \pm 1.58$	$1204^c \pm 30.25$
S8	$0.79^a \pm 0.07$	$10.37^f \pm 1.13$	$1100^a \pm 27.74$

Mean with the same letter in a column are statistically sig. at $p<0.05$

S_1 = point of discharge of waste water in to the drain, S_2 = 50m from point S_1, S_3 = 100m from S_1, and S_4 = the point of discharge of waste water in to River Gorax. S_5 = control 100m up the river. S_6 = 200m down the river from S_4, S_7 = 400m from S_4, S_8 = 600m from S_4.

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