



ORIGINAL ARTICLE

Physico-chemical Analysis of Pharmaceutical Effluent and Surface Water of River Gorax 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 S1 to S8. The levels of physical and chemical properties were simultaneously monitored in the effluent and the receiving watersheds over a period of 3 months using standard method of APHA, (1995).

This study investigated the physicochemical parameters in pharmaceutical effluent and surface water from River Gorax Maitumbi industrial layout Minna, Niger State, Nigeria. Samples were collected from eight points designated as S1 to S8. The physicochemical parameters determined showed highest pH value of 6.89 at S4 whereas the lowest pH value was at sample point S1. The highest temperature value of 46 (°C) was observed at S1 whereas the lowest value of 26°C was observed at S5; the highest electrical conductivity of 1673 ($\mu\text{S}/\text{cm}$) was observed at S1 whereas the lowest value was at S5; the lowest value of 11.02 (NUT) was observed at S5 while the highest was at S1 for turbidity; the highest value of 182 (mg/l) was observed at S7 for chemical oxygen demand and the lowest was at point S1. The anion values of 1.29 mg/l, 15.80 mg/l and 1767 mg/l were observed to be highest at S1 for phosphate, nitrate and chloride whereas the lowest values of 0.69 ± 0.05 mg/l, 7.21 mg/l and 950 mg/l were observed at S5. Most values observed at different sampling points were outside the compliance levels of the NSDWQ, FEPA and WHO tolerance limits for effluents discharge into receiving watersheds. 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: Pharmaceuticals, pollution, environment, AAS, Maitumbi, River, Industry.

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INTRODUCTION

Effluent is defined by the United States Environmental Protection Agency as "wastewater - treated or untreated - that flows out of a treatment plant, sewer, or industrial outfall. Generally refers to wastes discharged into surface waters" [1]. Pharmaceutical effluents are waste generated by pharmaceutical industry during the process of drugs manufacturing. 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 [2]. Toxic materials including many organic materials, metals (such as zinc, silver, cadmium, thallium, etc.) acids, alkalis, non-metallic elements (such as arsenic or selenium) are generally resistant to biological processes unless very dilute. Metals can often be precipitated out by changing the pH or by treatment with other chemicals. Many, however, are resistant to treatment or mitigation and may require concentration followed by land filling or recycling [3]. 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 [4].

Industrial effluents are characterized by their abnormal turbidity, conductivity, chemical oxygen demand (COD); total suspended solids (TSS) and total hardness. The effluent total hardness concentrations of a chemical-biological treatment plant were found greater than the influents. The results are presented in terms of the relative flux as a function of time related to hydrodynamic conditions and pollution characteristics of wastewater [5]. Industrial wastes and emission contain

toxic and hazardous substances, most of which are detrimental to human health [6]. 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 [7]. 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 [8]. 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 [9].

High levels of pollutants in river water causes an increase in biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), total suspended solids (TSS), toxic metals such as Cd, Cr, Ni and Pb and fecal coliform and hence make such water unsuitable for drinking, irrigation and aquatic life. It has been reported that TSS, BOD and COD in industrial effluents were above the permissible limits set by National Environmental Quality Standards for municipal and liquid industrial effluents (NEQS) [10]. Presently, some 2.4 billion people lack adequate sanitation and 3.4 million die each year in the world from water related diseases [11].

Pharmaceutical plants generate a wide variety of wastes during manufacturing, maintenance and housekeeping operations. While maintenance and housekeeping activities are similar from one plant to the next, the actual processes used in pharmaceutical manufacturing vary widely. With this diversity of processes comes a similar diverse set of waste streams. Typical waste streams include spent fermentation broths, process liquors, solvents, equipment wash waters, spilled materials and used processing aids [12]. The disposal of this type of wastes is of environmental concern. Minute concentrations of endocrine disruptors, some of which are pharmaceuticals, are having detrimental effects on aquatic species and possibly on human health and development [13]. Recently, there has been an alarming and worrisome increase in organic pollutants [14]. Since many effluents are not treated properly, these products are discharged on the ground or in the water bodies [15], and most of these discharges to water bodies accumulate in the system through food chain [15].

The uncontrollable growing use of pharmaceutical products now constitutes a new challenge. Most pharmaceutical effluents are known to contain varying concentrations of organic compounds and total solids including heavy metals such as Lead, Mercury, Cadmium, Nickel, Chromium and other toxic organic chemicals or phenolic compounds discharged from pharmaceutical industries are mutagenic and carcinogenic. Much attention has been paid to them since they have direct exposures to humans and other organisms [16]. According to a U.S. Geological Survey (USGS) study conducted back in [17], 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 [18].

Generally, pharmaceutical industries do not generate uniform waste streams, due to the variety of medicines produced during any given processing period [19]. 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 [20]. The presence of pharmaceutical chemicals in the environment is a matter of concern due to their lipophilic and non-biodegradability nature, as well as their biological activities [21].

Predicted impacts of the wastewater on the flora and fauna vary widely due to the wide variations in the characteristics of the wastewater [22]. Untreated or incompletely treated industrial wastewater contains algae materials, non – biodegradable organic matter, heavy metals and other toxicants that deteriorate the receiving stream [23]. Much work has been done in developing and testing newer techniques and their combinations for wastewater treatment [24]. The quality of these industrial effluents, thus, has substantial influence on the quality of surface water. Every effort should be made to replace highly toxic and persistent ingredients with degradable and less toxic ones. Measures to avoid the release of harmful substances should be incorporated in the design, operation,

maintenance, and management of the plant. Where appropriate, a pharmaceutical manufacturing plant should prepare a hazard assessment and operability study and also prepare and implement an emergency plan that takes into account neighboring land uses and the potential consequences of an emergency [25].

MATERIALS AND METHODS

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 $9^{\circ} 31^{\circ}$ N and longitude $7^{\circ} 00^{\circ}$ 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°C prior to analysis. Sampling and analysis of each parameter was conducted for three months from September to November 2012.

Laboratory analysis

Physicochemical parameters such as pH, DO, TDS, TSS, BOD, COD, conductivity and temperature were determined according to APHA [26]. pH and temperature ($^{\circ}\text{C}$) were measured In-situ, the conductivity meter, TSS and TDS meter and pH meter, were calibrated using HACH [28]. Dissolved oxygen (DO) meter was also calibrated prior to measurement with solution of 5%HCl in accordance with the manufacturer's instruction. Turbidity was determined using a standardized Hanna H198703 Turbidimeter, nitrate and phosphate concentrations were determined using DR/2010 HACH Spectrophotometer. New standards were created for each parameter during every measuring month.

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.

RESULTS AND DISCUSSION

Table 1: showed the variation of the physicochemical parameters analysed in the samples from Maitumbi pharmaceutical industrial layout and River Gorax in Minna. The concentrations of physical parameters in wastewater and surface water samples showed highest mean concentrations at point S_1 for all the parameters tested except for TSS which was observed to be higher at point S_6 and the pH which is more acidic at point S_1 . This can be attributed to high concentration of the effluent at the point of discharge as compared to the rest of the sampling points due to dilution.

The mean concentrations of the pH ranged from 5.65 ± 0.65 to 6.89 ± 0.12 The mean pH values are acidic, with sample point S_2 having the highest concentration of 5.65 ± 0.65 the effluent draining in to the River have increased it acidity from pH 6 to 5 which is above the [29] and [30] permissible limits of 6 to 8 for healthy habitation of aquatic organisms. Higher the acidity, the more soluble and mobile the metals become, and the more likely they are to be taken up and accumulated in plants [31].

Mean temperature at all sampling points were higher as compared to S_5 which is the control with mean of $26 \pm 0.34^{\circ}\text{C}$. It was observed that sample points S_1 have the highest mean temperature of 46.24 ± 3.41 which is above the [29] and [13] permissible limits of 40°C for wastewater discharged in to River. Effluent high temperature reduce solubility of oxygen and amplified odour due to anaerobic reaction [32].

Electrical conductivity is a function of total dissolved solids (TDS) known as ions concentration, which determines the quality of water [31]. Conductivity of water may also be useful indicator of

effluent salinity. The Electrical Conductivity ranged from 1062±96.67 to 1673±119.36 (µS/cm), it showed lowest value at point S₅ which is the control.

Turbidity is a very good test for water quality because it measures the cloudiness or haziness of fluid caused by particles that may not be visible to the naked eye. The Turbidity ranged from 11.02±1.05 to 28.78±1.18 (NTU), all the mean values observed for turbidity were above the [29] and [13] set limits of 5.00 NTU for wastewater discharge in to Rivers.

TDS value was observed to be highest at S₁ with value of 193.1 ± 5.35 mg/l as compared to the control at S₅ with 108.45 ± 4.65 mg/l. These values obtained for TDS in all the sampling points down the River were less than [29] and [13] standards of 1000 mg/l for the discharged of wastewater into surface water. It can be said that the industrial effluent discharged in to River Gorax may not be the main source of stream contamination but a contributing factor. Effluents with high TDS value may cause salinity problem if discharged to running water for irrigation [26].

The Total Suspended Solids (TSS) ranged from 29.67 ± 4.22 to 146.37±7.03 (mg/l). TSS value was observed to be highest at S₄ with value of 128.00 ± 16.19 mg/l as compared to the control at S₅ with 105.00 ± 14.06 mg/l. These values obtained for TSS in all the sampling points were lower than [29] and [13] standards of 500 mg/l for the discharged of wastewater into surface water.

Statistical analysis using ANOVA showed that there was significant difference between the eight sampling points for all the parameters analysed except for electrical conductivity (EC) which was not significantly different with all the parameters.

Table 1: Mean Concentration of Physicochemical Parameters in Pharmaceutical wastewater and surface water samples from River Gorax, Maitumbi industrial layout, Minna, Niger State, Nigeria

| Parameters | pH | Tempt. (°C) | E.C (µS/cm) | Tur. (NTU) | TDS (mg/l) | TSS (mg/l) |
|------------|----------------------------|--------------------------|-----------------------------------|-----------------------------|------------------------------|------------------------------|
| S1 | 5.90 ^a ±0.28 | 46 ^b ±3.41 | 1673 ^{abcdef} ±119.36 | 28.78 ^d ±1.18 | 193.05 ^e ±5.35 | 29.67 ^f ±4.22 |
| S2 | 5.65 ^a ±0.65 | 35 ^b ±2.87 | 1554 ^{abcdef} ±135.03 | 23.42 ^d ±1.06 | 148.32 ^e ±9.11 | 53.20 ^f ±3.54 |
| S3 | 6.12 ^a ±0.48 | 33 ^b ±2.16 | 157 ^{abcdef} ±115.84 | 17.73 ^d ±0.89 | 136.33 ^e ±5.83 | 101.00 ^f ±5.03 |
| S4 | 6.89 ^a ±0.12 | 32 ^b ±2.23 | 1305 ^{abcdef} ±138.69 | 17.22 ^d ±0.78 | 140.00 ^e ±7.23 | 123.03 ^f ±4.56 |
| S5 | 6.08 ^a ±0.48 | 26 ^b ±0.34 | 1062 ^{abcdef} ±96.67 | 11.02 ^d ±1.05 | 108.45 ^e ±4.65 | 99.43 ^f ±5.02 |
| S6 | 5.96 ^a ±0.24 | 30 ^b ±1.90 | 1177 ^{abcdef} ±193.18 | 15.33 ^d ±0.34 | 145.33 ^e ±4.72 | 146.37 ^f ±7.03 |
| S7 | 5.97 ^a ±0.38 | 29 ^b ±1.60 | 1141 ^{abcdef} ±121.29 | 14.87 ^d ±0.28 | 139.45 ^e ±2.32 | 116.74 ^f ±4.22 |
| S8 | 5.94 ^a ±0.38 | 27 ^b ±0.84 | 1138 ^{abcdef} ±118.32 | 14.09 ^d ±0.26 | 121.33 ^e ±1.88 | 102.35 ^f ±2.63 |

Mean with the same letter in a row are statistically not significant at P<0.05

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