PHYSICO- CHEMICAL CHARACTERISTICS OF PHARMACEUTICAL EFFLUENTS FROM SANGO-OTA, NIGERIA

Bukunola Oguntade (Dr.), Oluwafisayomi Babatola, Adewale Oderinde
Science Laboratory Technology Department, Federal Polytechnic, Ilaro
bukunola.oguntade@federalpolyilaro.edu.g; oluwafisayomi.babatola@federalpolyilaro.edu.ng

Abstract

Water plays a vital role in the day to day activities of man and over the years the quality of water bodies both in the rural and urban areas has received increasing research interest from scientists. The aim of this study was to investigate various physicochemical properties of pharmaceutical wastewater in Sango-Ota, Ogun state. Characterization of wastewater was evaluated in terms of temperature, pH, total suspended solids (TSS), total dissolved solids (TDS), Biochemical oxygen demand (BOD), Chemical oxygen demand (COD), and also to evaluate the presence of some heavy metals. The level of pollution of this effluent was compared with guidelines prescribed by World Health Organization (WHO) and The Federal Environmental Protection Agency (FEPA). The temperature ranged from 27.5-29 ^{o}C, pH ranged from 7.17-7.41, Total Alkalinity ranged from 259-289 mg/L, Chloride ranged from 5-10 mg/L, water hardness ranged from 350-365 mg/L, total suspended solids (TSS) ranged from 259-289 mg/L, total dissolved solids (TDS) ranged from 275-322 mg/L, Biochemical oxygen demand (BOD) ranged from 33-45 mg/L, Chemical oxygen demand (COD) ranged from 9-10 mg/L, Nitrates ranged from 8-9 mg/L, Phosphate ranged from 4.1-4.2 mg/L and dissolved oxygen (DO) ranged from 3-4 mg/L. The results of the heavy metals revealed that cadmium was not detectable, copper was within the acceptable limits according to FEPA with values ranging from 0.17 to 0.28 mg/L while iron and zinc were above the FEPA limits with values ranging from 33 to 35 mg/L and 1.48 to 1.53 mg/L respectively. This study reveals the need for the regulatory bodies to ensure that adequate effluent treatment methods are strictly adhered to by the pharmaceutical plants before their discharge to surface water to reduce their potential environmental hazards.

Keywords: Heavy metals, pharmaceutical effluents, environment, pollution, physicochemical.

Introduction

Industrial activities have expanded so much all over the world leading to the deterioration of the environment (Nivruti *et al.,* 2013). Pollution from industrial disposal and effluent discharges is a serious environmental issue in many developing countries of Africa (Uzoukwu *et al.*, 2004) including Nigeria. These discharges are done directly or indirectly into water bodies which are one of the most valuable natural resources for all living creatures on the earth. Water is essential for the sustenance of life as exemplified by its diversified uses such as drinking, cooking, washing, irrigation, farming, industrial activities and so on (Adigun, 2005). These industrial effluents have a hazardous effect on water quality, habitat quality, and complex effects on flowing water (Bound & Voulvolis, 2005).

The by-products of various industries such as textile, metal, dying chemicals, fertilizers, pesticides, cement, petrochemical, energy, power, leather, sugar processing, mining, and others are the main contributors to the surface and groundwater pollution in Nigeria (Iwuozor & Ekpunobi, 2018). A wide variety of wastes are generated by pharmaceutical industries 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 (Savita & Deepa, 2012). These effluents contain a high level of pollutants due to the presence of non-biodegradable inorganic matter such as heavy metals and other pollutants (Chelliapan *et al.*, 2011; Ramola & Singh, 2013). Although, effluents treatment plants are widely used in these industries to remove the effluents from the bulk drug, pharmaceutical compounds have been detected in treated effluent in concentrations ranging from µg/L to ng/L, possibly due to incomplete removal during the treatment process. This subsequently reaches wider water and soil environment through effluent discharge or sludge use (Daughton *et al.*, 1999). It is suspected that many of these toxic substances are potent carcinogens (Bredholt *et al.*, 2008).

Pharmaceutical companies are producing different types of pharmaceutical products at large scale and also producing complex non-biodegradable toxic wastes by-products and releasing untreated or partially treated wastes into the environment in the absence of strong regulations (Chander *et al.*, 2016).

Reports by the United States Geological Survey USGS (2002) also showed 80% of American streams were found to be contaminated with pharmaceutical drugs. Siyanbola *et al.* (2013) analyzed the physicochemical characteristics of industrial effluents in Lagos State, Nigeria, and found out that the pH of all the locations was above the FEPA limits and that the acidic nature of the industrial effluents is capable of stemming the pH of their respective receiving water bodies thereby, destabilizing fundamental properties such as alkalinity, metal solubility and hardness of the water. Hariharan *et al.* (2010) reported that temperature plays an important role in the biochemical reactions of aquatic organisms. Therefore, an increase in the temperature of the water body will promote chemical reactions in the water thereby promoting effects, such as bad odor and taste resulting due to non-solubility of gases. This research work aimed to determine the physicochemical properties of a pharmaceutical wastewater in Sango Ota Ogun state.

Materials and Methods

Collection of Sample

Pharmaceutical companies based in Sango-Ota, Nigeria, holding environmental certifications were selected to be partners in this work. Based on their commitment to the environment, the companies were visited to study their production process and the generation of effluents, as well as their respective waste-water treatment plants.

The effluent samples were collected from the drainage canals around the industries from the discharge points and were denoted as DP1 (point of discharge into the canal), DP2 (50 m away from discharge point) and DP3 (100 m away from the discharge point). The samples for the dissolved oxygen were collected in 300 ml BOD bottles avoiding contact with air and fixed on the spot, while samples for the physicochemical parameters were collected with plastic bottles pre-cleaned by washing with non-ionic detergents and rinsed with tap water.

Physiochemical Analysis

Samples for heavy metal were collected in pre-sterilized bottles and preserved with 5 ml concentrated nitric acid on site and refrigerated at 4 ^oC, prior analysis. pH was measured by the electrometric method using a laboratory pH meter model 31500 (expressway) while alkalinity, hardness, total dissolved solids, total suspended solids, phosphate, nitrate, sulphate, chloride, dissolved oxygen, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) were determined using the standard method described by American Public Health Association (APHA, 1999).

200 ml of well mixed sample solution was measured into a clean 500 ml evaporating dish. 2 ml of concentrated nitric acid was introduced into the sample solution and was evaporated on the water bath to less than 20 ml. The digested sample was further made to the 20 ml mark and stored in pre-cleaned 50 ml polyethylene bottles for analyses. This procedure was repeated for the blank but with distilled water. The metal content was determined by Atomic spectrophotometry (AAS) (Perkin Elmer, model 210). Metals determined included Iron (Fe), Copper (Cu), Zinc (Zn) and Cadmium (Cd). The analyses were done in triplicate and the mean values were obtained.

RESULTS AND DISCUSSION

Table 1 presents the physicochemical characteristics of the effluents from the different discharge points of the pharmaceutical industry into the environment. The results obtained were compared with the Federal Environmental Protection Agency (1991) permissible limits for effluents discharged into surface water and World Health Organization (2002) guidelines for drinking water recommendation.

Table 1: Mean values of the physicochemical parameters of the pharmaceutical industry effluents

Physicochemical parameter	DP1	DP2	DP3	FEPA	WHO
pH	7.41 ± 0.003	7.28 ± 0.003	7.17 ± 0.006	6.0-9.0	6.0-9.5
Temperature (^{O}C)	29.0 ± 0.289	32.0 ± 0.252	27.5 ± 0.058	< 40	36
Color	Cloudy	Cloudy	Colorless	NS	NS
Odor	Unpleasant	Unpleasant	Unpleasant	NS	NS
Conductivity **(**μScm^{-1}**)**	423.15±0.012	473.94± 0.003	495.66± 0.003	NS	NS
Appearance	Not clear	Not clear	Not clear	NS	NS
Alkalinity	162.0 ± 0.289	151.0 ± 0.333	140.0 ± 0.577	NS	NS
Chloride	10.0 ± 0.017	5.50 ± 0.058	5.0 ± 0.577	600	250
Total Hardness	350.32 ± 0.003	370.29 ± 0.003	375.28 ± 0.006	NS	NS
DO	3.60 ± 0.036	3.80 ± 0.058	4.10 ± 0.1	NS	NS
COD	10.10 ± 0.067	9.80 ± 0.153	9.40 ± 0.058	NS	NS
BOD	33.5 ± 0.029	40.0 ±0.289	45.5 ± 0.1453	50	NS
TDS	275.05 ± 0.026	308.06 ± 0.0003	322.18 ± 0.003	2000	< 1200
TSS	259.65 ± 0029	274.24 ± 0.003	289.02 ± 0.009	30	NS
Nitrate	9.53 ± 0.003	9.14 ± 0.003	8.82 ± 0.009	20	50
Phosphate	4.20 ± 0.003	4.18 ± 0.003	4.19 ± 0.009	5	NS
Iron	35.08 ± 0.009	33.72 ± 0.006	33.72 ± 0.003	20	NS
Zinc	1.53 ± 0.009	1.48 ± 0.003	1.48 ±0.003	< 1	0.01
Copper	0.28 ± 0.006	0.17 ± 0.006	0.17 ± 0.007	< 1	NS

*ND means non-detected

The colour and odour of industrial effluents are usually dependent on the type of industrial process carried out. In this study, the colours observed were from whitish to colourless and all the discharge points had an unpleasant odor.

pH is the hydrogen ion activity and a measure of acidity and alkalinity in aquatic bodies and it is one of the important biotic factors that serves as index for pollution (Sagar *et al.*, 2012). The principal component regulating pH in natural waters is the carbonate, which comprises CO_2, H_2CO_3, and HCO_3 (Benit and Stella, 2015). The pH ranged from 7.28-7.41 which are above the FEPA and WHO limits. David (2004) however, reported that if the pH value is above 7, this indicates that water is probably hard and contains calcium and magnesium ions. However, the pH values reduced as the discharge points were farther away from the point of discharge into the carnal.

Temperature is one of the most significant factors that affect the aquatic environment (Weqar *et al.*, 2012). The temperature ranged from 27.5-32.0 and is within the acceptable limits suggested by FEPA and WHO. Hariharan (2010) reported that biochemical reactions of aquatic organisms are temperature dependent.

Water conductivity is a useful indicator to determining the salinity of the effluent (Idris *et al.*, 2013). There is no FEPA limit for conductivity value, however the electrical conductivity values in this study ranged from 423.15-495.66 μScm^{-1}. The electrical conductivity values is dependent on the dissolved solids in the effluent as it was observed that as the conductivity values increased, the total dissolved solids (TDS) values also increased.

High alkalinity is a measure of wastewater strength. It shows the capacity of wastewaters to neutralize acids, and is undesirable. The alkalinity of water may be caused by OH^-, CO_3^{2-}, HCO^-_3 ions. Alkalinity is the estimate of ability of water to resist change in pH upon addition of acid (Boghra *et al.*, 2011). The high alkalinity values ranged from 140-162.0mg/L which could be as a result of the low DO values (Olaitan *et al.*, 2014**)** and it was also observed that they decreased from DP1 to DP3.

The presence of chloride in natural water can be attributed to the salt deposits, discharge of effluents from chemical industries, sewage discharges etc. Each of these sources may cause the local contamination of both surface and ground water (Boghra *et al.*, 2011). Chloride content in this study was found to be between 5mg/L to 10mg/L. This level of chloride content is below the FEPA standards.

Water hardness is a property of water which prevents the formation of lather with soap. Water containing $CaCO_3$ at low concentrations below 60 mg/L is generally considered as soft; 60-120 mg/L is moderately hard; 120-180 mg/L is hard; and more than 180 mg/l is very hard (McGowan, 2000). The water hardness in this study ranged from 350-365 mg/L and therefore can be categorized as very hard water which would require the use of chemicals for treatments.

The dissolved oxygen is a measure of the degree of pollution by organic matter, the destruction of organic substances, and the self-purification capacity of the water body, its values ranged from 3.6- 4.1 mg/L. This indicates that many high oxygen-demanding organic substances are manufactured by this pharmaceutical plant (Emongor *et al.*, 2005) and were discharged into the canals untreated or partially treated.

Biochemical oxygen demand (BOD) values ranged from 33-45 mg/L while chemical oxygen demand (COD) ranged from 9-10 mg/L. The values were within the FEPA limits. The biological oxygen demand (BOD) and chemical oxygen demand (COD) are useful parameters in water quality analysis and are both a function of DO. BOD directly influences the amount of DO in rivers and streams. The greater the BOD, the more rapidly oxygen is depleted in the water. This means that less oxygen is available to higher forms of aquatic life, which results in aquatic organisms becoming stressed, suffocating, and eventually dying (Lokhande *et al.*, 2011). It was also observed that as DO values decreased, COD and BOD values increased (Siyanbola *et al.*, 2011).

Total dissolved solids are a measure of total inorganic substances dissolved in water (Sonune *et al.*, 2015). The TDS values ranged from 275 mg/L - 322 mg/L which is within the FEPA and WHO acceptable limits.

Total dissolved solids/suspended solid are a measure of total inorganic substances dissolved/suspended in water. The total suspended solids affect the light intensity of water influencing turbidity and transparency (Tekade *et al.*, 2011).

Total suspended solids content in this study was found to be between 259 mg/L to 289 mg/L which is far greater than the FEPA standards. The higher values could be as a result of rain run-off water as the research was carried out in the rainy season (Dubey & Deepa, 2012).

The nitrate and phosphate content ranged from 8 to 9 mg/L and 4.18 to 4.20 mg/L, respectively. These values are lower than FEPA and WHO acceptable limits. Phosphates and nitrates are required in small amounts for growth and metabolism of plants and animals. However, these minerals can be harmful in excess quantities as it can cause algae bloom and reduction in the amount of oxygen in water thereby causing the death of aquatic animals (Ansar & Khad, 2005).

Of all the heavy metals accessed in this study, cadmium was the only metal that was not detected in any of the effluents. The concentrations of copper which ranged from 0.17 to 0.28 mg/L was below the FEPA and WHO standard while zinc and iron concentrations which ranged from 1.48 to 1.53 mg/L and 33.72 to 35.08 mg/L respectively were discovered to be higher than the WHO and FEPA standard. This could be attributed to iron being one the major raw materials used in this pharmaceutical company.

Conclusion

The results of this research revealed that some of the parameters (pH, TSS, iron and zinc) were above the permissible limits stipulated according to the regulatory bodies (FEPA and WHO). Hence, the continuous discharge of untreated or partially treated effluent into the surrounding environment may result in severe accumulation of the contaminants. This may be toxic to different organisms in that environment, the human beings and therefore should be discouraged for the sustainability of our environment. The regulatory bodies should also ensure strict compliance to the set limits.

References

Adigun, B. A. (2005). Water quality management in aquaculture and freshwater zooplankton production for use in fish hatcheries, *Journal of Environs*, 1(22), 1-3

Agedengbe, K., Akinwole, A., O., & Babatunde, A., O. (2003). Effluents characteristics of selected industries in western Nigeria and implications for re-use in agricultural production. *Journal of Environs*, *4* (1) 79-82.

Ansar, A.& Khad, F. (2005). Eutrophication: An Ecological Vision. *The Botanical Review*, *71*(4), 449-82.

APHA, (1992). Standard Methods of Water and Wastewater Examination 18th Ed. American Public Health Association, NY. Washington DC. 2-172.

Benit, N. & Stella-Roslin, A. (2015). Physicochemical properties of wastewater collected from different sewage sources. *International Journal of Innovative Science, Engineering & Technology*, *2* (11), 2348 – 7968.

Boghra, R. J., Kothawade, P. C., Belgamwar, V.S., Nerkar, P. P., Tekade, A. R. & Surana, S. J. (2011). Solubility, Dissolution Rate and Bioavailability Enhancement of Irbesartan by Solid Dispersion Technique. Chemical and Pharmaceutical Bulletin, *59*, 438-441.

Bredholt, H., Fjaervik, E., Johnsen, G., & Zotchev, S. (2008). Actinomycetes from Sediments in the Trondheim Fjord, Norway: Diversity and Biological.Activity. *Journal of Marine drugs*, *6*, 12-24.

Chander, V., Sharma, B., Negi, V., Aswal, R., Singh, P., Singh, R., & Dobhal, R. (2016). Pharmaceutical compounds in drinking water. *Journal of Xenobiotics*, *6*(1), 5774.

Chelliapan S., Thomas W., Ali Y., & Paul, J., S. (2011). Influence of organic loading on the performance and microbial community structure of an anaerobic stage reactor treating pharmaceutical wastewater. *Journal of Desalination*, *1*(271), 257-264.

Daughton, C. G., & Ternes, T. A. (1999). Pharmaceuticals and personal care products in the environment: agents of subtle change. *Environmental Health Perspectives, 107*, 907-938.

Dubey, S. & Deepa, D. (2012). Analysis of Effluent Using Physico-Chemical Parameters at Pharmaceutical Industries.*CIBTech Journal of Pharmaceutical Sciences, 1*(2-3), 24-27.

Emongor, V., Kealotswe , E., Koorapetse, I., Sankwansa, S., & Keikanetswe, S. (2005). Pollution indicators in Gaberone effluent. *Journal of Applied Science, 5*, 147-150.

Ezenobi, N. O., & Okpokwasili, G., C. (2004). Bacterial flora and Physiochemical Characteristics of Hospital Sewage in Port-Harcourt City, Nigeria. *International Journal of Environmental Studies*, *54*(2), 145-152.

Idris, M. A., Kolo, B. G., Garba, S. T.& Ismail, M. A. (2013). Physico-chemical Analysis of Pharmaceutical Effluent and Surface Water of River Gorax in Minna, Niger State, Nigeria. *Bulletin of Environment, Pharmacology and Life Sciences*, *2*(3), 45-49.

Iwuozor K. O., & Ekpunobi E. C. (2018). Physico-Chemical Parameters of Industrial Effluents from a Brewery Industry in Imo State, Nigeria. *Modern Chemistry, 6*(4), 50-55.

Kolpin, D. W., Edward T. F., Michael T. M. E., Michael T., Steven D. Z., Larry B. B., & Herbert T. B. (2002). Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams: A National Reconnaissance. *Environmental Science Technology, 36*(6), 1202–1211.

Lokhande, R. S., Singare, P. U., & Pimple, D. S. (2011). Study on Physico-Chemical Parameters of Waste Water Effluents from Taloja Industrial Area of Mumbai, India. International Journal of Ecosystem, *1*(1), 1-9.

McGowan, W. (2000). Water processing: residential, commercial, light-industrial, 3rd ed. Lisle, IL, Water Quality Association

Nivruti, T., Nirgude, S. S., & Venkatachalam A. (2013). Physico-Chemical Analysis of Some Industrial Effluents from Vapi Industrial Area, Gujarat, India. Rasayan. *Journal of Chemistry*, *6*(1), 68-72.

Olaitan, O. J., Sulola, E. O., Kasim L. S. & Daodu, J. O. (2014). Physico-Chemical Characteristics of Pharmaceutical Effluents from Sango Industrial Area, Nigeria. *Bulletin of Environment, Pharmacology and Life Sciences, l3*(10), 78-81.

Ramola B., & Singh A. (2013). Heavy Metal Concentrations in Pharmaceutical Effluents of Industrial Area of Dehradun (Uttarakhand), India. *Journal of Environmental Analysis and Toxicology, 3, 173.*

Sarwar, S. K., & Majid, U. I. (1997). Abiotic features and diatom population of Wular lake, Kashmir. *Ecol. Env. Cons, 3*(3), 121-122.

Savita, D., & Deepa, D. (2012). Analysis of Effluent using Physico-Chemical Parameters at Pharmaceutical Industries. *Journal of pharmaceutical sciences*, 1,(2-3) 24-27.

Siyanbola, T. O., Ajanaku, K. O., James, O. O., Olugbuyiro, J. A. O., & Adekoya J. O. (2011). Physico-Chemical Characteristics of Industrial Effluents in Lagos State, Nigeria. *Pure and Applied Science, and Technology*, *1*, 49-54

Sonune, N. A., Mungal, N. A., & Kamble, S. P. (2015). Study of physico-chemical characteristics of domestic wastewater in Vishnupuri, Nanded, India. *International Journal of current microbiology and applied sciences*, *4*(1), 533-536.

USEPA, (2006). United States Environmental Protection Agency.

Uzoukwu, B. A., Ngoka, C., & Nnaji, N. (2004). Monthly Variation of the Physicochemical Properties of Effluents from Rimco Industries, Nnewi, Nigeria. *Global Journal of Pure and Applied Sciences*, *10*(1), 203-210.