



Physico-chemical parameters of industrial effluents from a starch-mill industry in Anambra State, Nigeria

Iwuzor Kingsley Ogemdi^{1*} and Ekpunobi Emmanuel Chidubem²

¹Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University, Awka, Nigeria

²Department of Microbiology, Abia State University, Abia State, Nigeria
kingsleyiwuzor5@gmail.com

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Abstract

Environmental pollution is one of the chief causes of sickness in our society. Industrial effluents unfortunately have their final destinations in streams, which serve as the main source of water supply to most rural communities. There is need to monitor the effluents discharged by industries to ensure that they comply with regulatory standards. This work examined some physicochemical parameters of effluents from a Starch-mill Industry in Anambra state. This company discharged effluents in non-compliance with the Nigerian National Regulations as confirmed from the Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Electrical Conductivity (EC), Nitrogen, and Turbidity results from this research. The heavy metals except Lead and Copper had concentrations that were within WHO/FEPA limits. The Lead (Pb) and Copper (Cu) concentrations of the Starch Mill was above the WHO and FEPA standards. The other heavy metals have concentrations that were within WHO/FEPA limits. These confirmed results posed health risks to several rural communities which rely on the receiving water bodies as their primary source of domestic water. There is need for the intervention of appropriate regulatory agencies to ensure production of high quality treated final effluents. This scenario is typical of most industries in developing nations where enforcement of environmental regulations are deficient. To avoid pollution, Regulatory Authorities should closely monitor compliance by industries.

Keywords: Effluent, physicochemical, starch-mill, biochemical oxygen demand (BOD), chemical oxygen demand (COD), electrical conductivity (EC), nitrogen, turbidity.

Introduction

Effluent is defined as liquid waste flowing out of a factory, farm, commercial establishment, or a household into a water body such as a river, lake, or lagoon. The United States Environmental Protection Agency defines effluent as wastewater treated or untreated that flows out of a treatment plant, sewer, or industrial outfall^{1,2}.

In various under-developed countries, untreated sewage and industrial effluents are utilized for the cultivation of crops and vegetables. It is a common practice in Nigeria where farmers suppose it as a source of irrigation and nutrients for cultivation while administrators assume it a low cost method of disposal. Unprocessed effluents contain heavy metals, microorganisms and organic pollutants. Problems arise due to the increase of metal ions in biosphere with continuous application onto soils. These metals have toxic impact on metabolism of living organisms when they exist beyond their respective safe limits in soils, vegetables and crops. They get their way, through food chain, in the bodies and produce health hazard effects on animals and human beings³. The uncontrolled discharge of waste effluents into water bodies also has harmful effects both on water quality and aquatic life. Effluent can alter the physical, chemical and biological nature of receiving water body⁴. The

initial effect of waste water is to degrade physical quality of the water. Later biological degradation becomes evident in terms of number, variety and organization of the living organisms in the water⁵. Effluents are composed mainly of either organic, inorganic matter or both and toxic substances depending on its source. Inorganic matter in effluent are composed of various chemical containing nitrogen, phosphorus and potassium. These elements especially phosphorus stimulates the growth of microscopic plants while nitrogen promotes overgrowth of aquatic vegetation which degrades water quality. Potassium promotes productivity of aquatic animals such as fish⁶.

Pollution is the introduction of contaminants into the natural environment that brings about adverse changes to the environment. The Federal Environmental Protection Agency defines pollution as man - made or man - aided alteration of chemical, physical or biological quality of the environment to the extent that is detrimental to that environment or beyond acceptable limits. There are seven types of pollution i.e. Land Pollution, Air Pollution, Noise Pollution, Water Pollution, Radioactive Pollution, Industrial Pollution and Thermal Pollution. With rising pollution levels in the country, life has become endangered. Water, Air and Sound pollution are making people injurious, leading to sicknesses and untimely deaths. There are various laws to manage the pollution yet these laws

are not properly executed; hence this problem has enlarged day by day. It is essential to clean the dirty waters of different industries so as to improve the quality of life and assure longevity⁸.

The Sources of pollution include; i. Industrial discharge, ii. Agricultural practices, iii. Natural disaster, iv. Domestic wastes, v. War and explosives.

In plain language, a pollutant is the residue of things we make, use and throw away. Pollutant could be the waste product or by-product of the manufacturing process or a misapplied useful product. Examples of such type include discarded household property, industrial aqueous discharge (effluents), spilled fertilizers, pesticides or petroleum and farm garbage. The principal impurities examples sulphides, phenols, inorganic acids, etc. are usually contained in the pollutants. Usually the physio-chemical composition of the impurities determines the effect of aqueous discharge in water. Prominent among these factors are the industrial effluents⁹.

Air pollution is a sign of disorder to the composition of chemicals/particulates and excess emission of gases/vapors in the atmosphere. Approximately, 57% pollution rate is caused by Automobile and 20% is due to released gasses from industries. Global warming, ozone layer depletion, smog and acid rain are some of the major aftereffects of air pollution. Carbon and nitrogen cycles are necessary for regulating the composition of gases in the environment. The common sources that escort to air pollution are the fuel gases from garbage burning, exhaust gases from industries/ auto-motives, biological decay, forest fire, volcanic eruptions, building demolition/construction and municipal waste disposal¹⁰.

Water pollution is the contagion of water by foreign particles, pathogenic germs, toxic materials, substances that involve much oxygen to decompose, radioactive stuff, easy soluble substances, etc., which deteriorates the quality of the water and interfere with the condition of aquatic environment. Water pollution occurs in lakes, oceans, streams, underground water, rivers, bays, etc. The main pollutants of water bodies are heavy metals, sewage, sediment/infectious organisms, synthetic agricultural chemicals and organic matter¹¹.

Land pollution occurs mostly due to the untreated sewage, accumulation of solid waste, alteration/imbalance of soil chemical composition, deposition of non-biodegradable materials, modification of chemicals into poisons, pesticides and fertilizers. Due to land pollution, there is a huge damage of land and topsoil per year. Moreover, there is a loss of cultivated land to overuse and mismanagement. The bases for such destruction are usually due to non-idealistic soil management methods and indecent cultivation practices. The important causes of land pollution are mining / quarrying, buildings demolition / constructions, municipal / industrial / agriculture wastes etc¹².

Noise is a frequent problem in modern-day life and it represents a severe threat to worth of life. Due to Noise pollution, many people are prone to serious health hazards. Noise creates shocking impact on man's brain. Due to the increase in the utilization of heavy-duty machineries and vehicles, the prescribed pollution is still increasing day by day. Noise levels are calculated by various methods such as decibel method, traffic noise index, community noise equivalent level, noise rating, noise pollution level and sound pressure level. Industrial noises, road traffic noise, rail traffic, air traffic and neighborhood/domestic noises are the major sources of noise pollution¹².

Nuclear energy is released by the fission or fusion reactions of atoms. It is used to generate electricity and nuclear weapons. Nuclear waste is a radioactive pollution because it emits ionizing radiations such as Alpha, Beta and Gamma. The main sources that escort to radioactive pollution are nuclear power plants, nuclear weapon, uranium mining and nuclear waste disposal¹².

Thermal Pollution is the most recent pollution, which is increasing day by day. Heat produced from industries and the increases of the environmental temperature are two main contributors of this pollution. Due to the pollution, the ozone layer has been damaged and hence global warming impact becomes more intense¹².

The haphazard discharge of different types of industrial effluents along with hazardous waste has resulted in severe environmental pollution through the deterioration of the ecosystem in Nigeria. Poisonous industrial chemicals can be identified in the groundwater of many industrial cities of Nigeria. There is no appropriate monitoring system of industrial effluents and there is an insufficient record of the nature of effluents, their magnitude and composition. A systematic/comprehensive survey has not been conducted for the industrial sources, volumes and characteristics of industrial effluents in Nigeria. However, partial investigations of particular sources and observations have shown significance of the industrial pollution in a number of locations. Only few industries have treated their effluents according to the recommended standards. The remainders simply release their effluents in the most convenient way. These effluents are the major source of pollution. Soils adjacent to the industries and the cultivated crops/vegetables become polluted extensively. So there is a need for their checks and balances. The main industries producing environmental hazards are the manufacturer of chemicals, cement, textiles, pharmaceuticals, pulp and paper, leather tanning and petroleum refining¹⁶.

The aim of this study is to analyze the physicochemical compounds and metal concentrations in the effluents generated by a Starch-mill industry in Anambra state, Nigeria. The results from the analyses will be compared with reference standards to ascertain its compliance with regulatory standards.

Materials and methods

Collection of sample: The company uses raw cassava to manufacture starch and other starch based products. The effluent samples were collected from the points of discharge of the company. 250ml glass bottles were used to collect samples for COD and BOD while samples for the physicochemical parameters were collected with plastic bottles pre-cleaned by washing with non-ionic detergents and rinsed with tap water.

Physicochemical analysis: All field meters and equipment were checked and calibrated according to the manufacturer's specification. pH, temperature, transparency and depth were determined while on site. Other parameters including heavy metals were analyzed in the laboratory.

Determination of pH: Method: pH was measured by electrometric method using laboratory pH meter Hanna model HI991300.

Procedure: i. The electrodes were rinsed with distilled water and blot dry. ii. The pH electrodes were then rinsed a small beaker with a portion of the sample. iii. Sufficient amount the sample was poured into a small beaker to allow the tips of the electrodes to be immersed to a depth of about 2cm. The electrode was at least 1cm away from the sides and bottom of the beaker. iv. The temperature adjustment dial was set accordingly. v. The pH meter was turned on and the pH of the sample recorded.

Determination of Electrical Conductivity: Analysis was carried out according to American Public Health Association 2510 B guideline Model DDS-307.

Procedure: i. The conductivity cell was rinsed with at least three portions of the sample. ii. The temperature of the sample was then adjusted to $20 \pm 0.1^\circ\text{C}$. iii. The conductivity cell containing the electrodes was immersed in sufficient volume of the sample, iv. The conductivity meter was turned on and the conductivity of the sample was recorded.

Determination of Total Dissolved Solids (TDS): Method: Total dissolved solids was determined using APHA 2510 A TDS 139 tester.

The fiber filter disc was prepared by placing it, wrinkled side up in the filtration apparatus. Vacuum was applied and the disc washed with three successive 20ml washings of distilled water. A clean evaporating dish was heated to $180 \pm 2^\circ\text{C}$ in an oven for one hour, cooled and stored in a desiccator until needed. It was weighed immediately before use. A sample volume was chosen to yield between 2.5-200mg dried residue. 50ml of well mixed sample was filtered through the glass-fiber filter and it was washed with three successive 10ml volumes of distilled water, allowing complete draining between washings. Suction was continually applied for about three minutes after filtration was complete.

Filtrate was transferred to a weighed evaporating dish and evaporated to dryness on a steam bath. The evaporating dish was finally dried for at least one hour in an oven at $180 \pm 2^\circ\text{C}$, cooled in a desiccator to and was weighed.

Calculation:

$$\text{TDS} = (A-B) * 10^3 \text{ mg/l}$$

Where: A = weight of dish + solids (mg), B = Weight of dish before use (mg)

Determination of Water Hardness: Method: Hardness was measured using standard analytical method of APHA.

Procedure: 50cm^3 of the water sample was introduced into a beaker and 1cm^3 buffer solution of NH_3 added. Three drops of solochrome Black T indicator was also added and the solution swirled properly. The mixture was titrated with 0.01 EDTA solution until it changed from wine red to pure blue with no bluish tinge remaining. The total hardness of the water sample was calculated.

$$\text{Total hardness} \left(\frac{\text{mg}}{\text{CaCO}_3} \right) = \frac{\text{volume of titrant} \times 100}{\text{Volume of sample (Cm}^3)}$$

Determination of Nitrate: Method: Nitrate was determined using a PD303 UV spectrophotometer.

Procedure: A known volume (50ml) of the sample was pipetted into a porcelain dish and evaporated to dryness on a hot water bath. 2ml of phenol disulphonic acid was added to dissolve the residue by constant stirring with a glass rod. Concentrated solution of sodium hydroxide and distilled water was added with stirring to make it alkaline.

This was filtered into a nessler's tube and was made up to 50ml with distilled water. The absorbance was read at 410nm using a spectrophotometer after the development of colour. The standard graph was plotted by taking concentration along X-axis and the spectrophotometric readings (absorbance) along Y-axis. The value of nitrate was found by comparing absorbance of sample with the standard curve and expressed in mg/l.

Methods for Calibration: Standard nitrate solution was prepared by collecting 50ml of the stock solution, 2ml of phenol disulphonic acid added and diluted to 500ml, to give 1ml $10\mu\text{g}$. The solution of various strengths ranging from 0.0 (blank) to 1.0 mg/l at the intervals of 0.2mg/l was prepared by diluting stock solution with distilled water.

Determination of Phosphate: Method: Phosphate was measured using 4500-P B.5 and 4500-PE.

Procedure Exactly 100ml of the homogenized and filtered sample was pipetted into a conical flask. The same volume of distilled water (serving as control) was also pipetted into another conical flask. 1ml of 18M H_2SO_4 and 0.89g of ammonium persulphate were added to both conical flasks and

gently boiled for 1½ hours, keeping the volume of 25-50cm³ with distilled water. It was then cooled, one drop of phenolphthalein indicator was added and after being neutralized to a faint pink colour with 2M NaOH. The pink colour was discharged by drop wise addition of 2M HCl, and the solution was made up to 100ml with distilled water. For the calorimetric analysis, 20ml of the sample was pipetted into test tubes, 10ml of the combined reagent added, shaken and left to stand for 10 minutes before reading the absorbance at 690nm in a spectrophotometer, using 20ml of distilled water plus 1ml of reagent as reference.

Table-1: Preparation of Standard Calibration Curve for Nitrate Determination.

Standard Solution (ml)	Distilled Water (ml)	Concentration (mg/l)	Absorbance
0.00	1.00	0.00	0.00
0.20	0.80	0.002	0.004
0.40	0.60	0.004	0.012
0.60	0.40	0.006	0.017
0.80	0.20	0.008	0.020
1.00	0.00	0.010	0.026

Method for Calibration: Standard phosphate solution: 219.5 mg of dried AR potassium hydrogen phosphate was dissolved in distilled water and made up to 1000ml, 1ml=50.0µg of phosphate. 10ml of the stock solution was made up to 1000ml to give 1ml =0.05mg. Standards of strength ranging from 0 (blank) to 0.05mg/l at intervals of 0.01mg is prepared by diluting the stock with distilled water.

Table-2: Preparation of Standard Calibration Curve for Phosphate Determination.

Standard Solution (ml)	Distilled Water (ml)	Concentration (mg/l)	Absorbance
0.00	1.00	0.00	0.00
0.20	0.80	0.001	0.032
0.40	0.60	0.002	0.048
0.60	0.40	0.003	0.066
0.80	0.20	0.004	0.075
1.00	0.00	0.05	0.088

Determination of Chloride: Method: Chloride was analyzed according to EPA standard method.

Procedure: A 100ml of the clear sample was pipetted into an Erlenmeyer flask and the p^H adjusted to 7-10 with either H₂SO₄ or NaOH solution. Then 100ml of K₂CrO₄ indicator solution was added with standard solution of AgNO₃ in a permanent reddish brown coloration. The AgNO₃ titrant was standardized and a reagent blank established. A blank of 0.2-0.3ml was usually used.

Calculation;

$$\text{Chloride concentration} = \text{Titre value (x)} \times 10 = 10\text{mg/l.}$$

Determination of Sulphate: Method: sulphate was analyzed according to APHA standard method.

Procedure: 250cm³ of the water sample was evaporated to dryness on a dish. The residue was moistened with a few drops of concentrated HCl and 30 cm³ distilled water was added. This was boiled and then filtered.

The dish was rinsed and the filter paper was washed with several portions of distilled water and both filtrate and washings were added together. This was heated to boiling and then 10cm³ of 10% BaCl₂ solution was added, drop by drop with constant stirring. The mixture was digested for about 30 minutes, filtered and the filter paper was washed with warm distilled water. It was then ignited, cooled and weighed in an already weighed crucible.

Calculation

$$\text{Mg/dm}^3 \text{ SO}_4^{2-} = \text{mg BaSO}_4 \times 411.5 \text{ cm}^3 \text{ of water sample.}$$

Analysis of Heavy Metals: Heavy metal analysis was conducted using Varian AA240 Atomic Absorption Spectrophotometer according to the method of American Public Health Association.

Principle: Atomic absorption spectrometer's working principle is based on the sample being aspirated into the flame and atomized when the AAS's light beam is directed through the flame into the monochromator, and onto the detector that measures the amount of light absorbed by the atomized element in the flame. Since metals have their own characteristic absorption wavelength, a source lamp composed of that element is used, making the method relatively free from spectral or radiation interferences. The amount of energy of the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample.

Procedure: The sample was thoroughly mixed by shaking, and 100ml of it is transferred into a glass beaker of 250ml volume, to which 5ml of concentrated nitric acid is added and heated to boil till the volume was reduced to about 15-20ml, by adding conc. nitric acid in increments of 5ml till all the residue is completely dissolved. The mixture was cooled, transferred and made up to 100ml using metal free distilled water. The sample was aspirated into the oxidizing air-acetylene flame. When the aqueous sample was aspirated, the sensitivity for 1% absorption was observed. (Table-3 shows the instrumental parameters).

Table-3: Instrument (AAS) Settings.

Metal	Wavelength	Flame type	Uptake time
Lead	217.0nm	Air/acetylene	5sec
Iron	248.3nm	Air/acetylene	5sec
Zinc	213.9nm	Air/acetylene	5sec
Copper	324.7nm	Air/acetylene	5sec
Silver	302.5nm	Air/acetylene	5sec
Arsenic	193.7nm	N ₂ O/acetylene	5sec
Magnesium	285.2nm	Air/acetylene	5sec
Calcium	422.7nm	N ₂ O/acetylene	5sec
Sodium	589.0nm	Air/acetylene	5sec
Potassium	766.5nm	Air/acetylene	5sec
Iron	248.3nm	Air/acetylene	5sec

Results and discussion

The results of the analysis of the physicochemical Parameters are summarized in Table-4.

Table-4: Physicochemical Results of Sample.

Parameter	Starch-Mill Industry
Conductivity (µs/cm)	1727
pH	4.05
Turbidity (NTU)	848
TDS (ppm)	392
Hardness (ppm)	2500
Nitrate (mg/l)	0.306
Phosphate (mg/l)	0.357
Chloride (mg/l)	4.3
Sulphate (mg/l)	75
BOD (mg/l)	328
COD (mg/l)	174

Table-5: Elemental Analysis Results of Effluent Samples.

Parameter	Starch-mill industry
Cadmium (ppm)	0.156
Cobalt (ppm)	0.978
Lead (ppm)	1.30
Copper (ppm)	1.205
Chromium (ppm)	0.00
Iron (ppm)	0.00
Magnesium (ppm)	1.6166
Nickel (ppm)	0.009
Manganese (ppm)	0.045
Zinc (ppm)	0.045

Discussion: The result of the physicochemical analysis of the industrial effluents (Table-4) showed a wide variation in comparison with the approved standard set by the Federal Environmental Protection Agency¹⁰.

Conductivity of water is used as a measure of the total concentration of ionic species or salt content. Though there is no FEPA guideline for conductivity value, the South African guideline for conductivity in effluent that will be discharged into river is 250µS m⁻¹. The effluent conductivity value of the company was above this acceptable limit. High conductivity values of effluents can increase the salinity of the receiving river, which may result in adverse ecological effects on the aquatic biota. Such high salt concentrations hold potential health hazards¹⁵. The pH value of the Starch-Mills (4.05) Industry was very low when compared with FEPA approved limit of 6-9. Since pH is a function of hydrogen ion concentration (i.e., pH = -log [H⁺]), the high acidity of the effluents was probably due to high concentration of hydrogen ion [H⁺] in the effluents. When effluents with low pH have their ways into water bodies, it causes growth inhibition of bacteria species in the receiving water body.

The BOD values of the company exceeded the FEPA approved limit of 50mg L⁻¹. High BOD values are hazardous for the survival of the aquatic biota in the receiving stream because oxygen is utilized by aquatic species to oxidize organic matter: CH₂O + O₂ = CO₂ + H₂O. BOD represents the amount of oxygen utilized when the organic matter in a given volume of water is degraded biologically. It is a measure of the productivity of a particular water body. Any water body with has high BOD value, is starved of oxygen and needs more oxygen to completely degrade the organic life in it.

The value of Total Dissolved Oxygen (TDS) for the Starch-Mill industry is within the limit stated by FEPA (2000ppm). TDS is a measure of the combined content of all organic and inorganic substances contained in water. However, TDS is not generally considered a primary pollutant (i.e. it is not deemed to be associated with health effects), it is used as an indication of aesthetic characteristics of drinking water and as an aggregate indicator of the presence of a broad array of chemical contaminants.

Chemical Oxygen Demand COD for the company was very high (more than two times the FEPA limit of 80ppm). This showed that the effluents were seriously contaminated with organic pollutants, since COD is indirectly used to measure the amount of organic compounds in water.

Turbidity is a measure of the degree to which water loses its transparency due to the presence of suspended particulates; the more total suspended solids in water, the murkier it seems and the higher the turbidity. The turbidity of the effluents of the Starch-Mill industry was 848NTU. This figure is exceedingly high compared to the turbidity limit of 5NTU for drinking water as stipulated by FEPA (though the limit for effluents was not stated). The suspended particles absorb heat from the sunlight, making turbid waters become warmer, and so reducing the concentration of oxygen in the water. The suspended particles also scatter the light, thereby decreasing the photosynthetic activities of aquatic plants and algae.

The hardness of the industrial effluent was 2500ppm for the Starch-Mill Industry. This figure was very high compared with the 200ppm permissible limit for drinking water. Hard drinking water is generally not harmful to health, but can cause calcification of taps, boilers, kettles and other equipment used for handling water. Hard water is characterized by high mineral content; in domestic settings, hard water is often indicated by a lack of suds formation when soap is agitated in water.

The values of other physico-chemical parameters (nitrate, phosphate, chloride and sulphide) for the Starch-Mill Industry fell within the approved limit set by the FEPA, 1991. 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.

When sulphates exceed the recommended limit, it can have a negative impact on public health, potentially causing diarrhea which can be more of a problem in infants, the elderly and people with underlying health conditions. Chlorine on the other hand causes environmental problems and it is also harmful to living organisms in water and in the soil.

The accumulation of metals in an aquatic environment has direct consequences to man and to the ecosystem. Some metals

like Zn and Cu are needed for metabolism in organisms. Interest in such metals lies in the thin line between their toxicity and essentiality. Some metals like Al, Cd and Pd are extremely toxic even at trace levels.

From the results of the elemental analysis of the industrial effluent of the company, the values for Cd, Co, Cr, Fe, Mg, Ni, Mn and Zn fell within the range of the limit set by FEPA, 2012. The concentrations of Lead and Copper in the effluents of the Starch-Mill industry were above the range of FEPA approved limit of less than 1ppm.

Lead in drinking water can cause a variety of adverse health effects. In babies and children, exposure to lead in drinking water above the action level can result in delays in physical and mental development, along with slight deficits in attention span and learning abilities. In adults, it can cause increase in blood pressure. Adults who drink this water over many years could develop kidney problems or high blood pressure.

Some people who drink water containing copper in excess may with short term exposure experience gastrointestinal distress, and with long term exposure may experience liver or kidney damage.

Conclusion

The study has shown that the Starch-Mill Industry effluents had their BOD, COD, EC, Turbidity and Colour above the required WHO/FEPA standards. Lead (Pb) and copper in the Starch-Mills were quite above WHO/FEPA standards for effluents discharge. This undoubtedly has negative impacts both on the environment and living things including human beings.

Since the results of analyses have shown that the Starch-mill Industry effluents are not well treated, it has been recommended that Regulatory agencies of states and Nigeria should monitor and ensure compliance of proper effluent treatment by industries.

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