



Determination of levels of Physicochemical Parameters and Organic Contaminants in Effluents from a Food Processing Industry in Port Harcourt, Nigeria

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Abstract The study was carried out to determine the levels of physicochemical parameters, heavy metals and organic contaminants like PAHs and n-alkanes presents in effluent of a food processing industry in Port Harcourt. Duplicate effluent samples were taken for 3 days and preserve using HNO_3 . Acid digestion and liquid extraction was carried out before extractants/filtrates were analyzed using Atomic Absorption Spectrometer and Gas Chromatography. The level of some physicochemical parameters was pH (5.98 ± 0.056), Nitrate ($5.94 \pm 0.008 \text{mg/l}$), Turbidity ($7.43 \pm 0.053 \text{NTU}$), TSS ($146.32 \pm 0.026 \text{mg/l}$) electrical conductivity ($106.33 \pm 0.046 \mu\text{s/cm}$), Phosphates ($4.332 \pm 0.003 \text{mg/l}$). Heavy metal concentrations were in the order $\text{Cd} (0.49) > \text{Cu} (0.194) > \text{Zn} (0.18) > \text{Mn} (0.071 \text{mg/l}) > \text{Fe} (0.014) > \text{Cr} (0.013)$. The concentration of heavy metals in the effluent samples were below the World Health Organisation standard except for Cadmium. There was presence of high molecular weight n-alkanes (142.7mg/l for C17-C32). The total PAHs concentration was 197.5mg/l with nine of them identified. The PAHs identified were more of higher molecular weight than the lower molecular weight PAHs. The study result revealed that the PAHs in the effluent of the food processing industry was both from petrogenic (petroleum) and pyrogenic (combustion). There is need for adequate treatment of the effluent before being discharged into water body to avert possible pollution of the aquatic system. This could be detrimental to the biotas and humans using such water for domestic purpose and could lead to bioaccumulation in the sediment of the river.

Keywords Physicochemical Parameters, Organic Contaminants, Effluents, Food Processing Industry

Introduction

Water is an indispensable natural resource without which there would have been no life on earth. The importance of water to man cannot be overemphasized. Man can survive longer without food than without water. Water is freely available through rainfall and other components of the hydrologic cycle. Until recently, man has tended to take this abundant natural resource for granted.

Man exerts many effects which directly or indirectly affects his environment affects his environment. The development of industries and extensive urbanisation means increased water consumption and pollution resulting from problems of waste disposal. Unfortunately, in most developing countries like Nigeria, effluent quality standards imposed by legislation (where they exist) are sometimes easily flouted [1].

In most developing countries like Nigeria, most industries dispose of their effluents without treatment. These industrial effluents have a hazardous effect on water quality, habitat quality, and complex effects on flowing waters [2]. Industrial wastes and emissions contain toxic substances which are detrimental to human health [3-5].



The world global growth and rapid industrial development have led to the recognition and increasing understanding of the interrelationship between pollution, public health and the environment. While almost all industrial activities cause some pollution and produce waste, relatively few industries (without pollution control and waste treatment facilities) are responsible for the bulk of the pollution.

Industrial effluents are liquid wastes that are produced during industrial activities. Over the years, the improper disposal of industrial effluents has been a major problem and a source of concern to both government and industrialists. In most cases, the disposal, or discharges of effluents, even when there are technologically and economically achievable for standards, do not always comply with pre-treatment requirement and with applicable toxic pollutant effluent limitation or prohibitions. The consequence of these anomalies is a high degree of environmental pollution leading to serious health hazards [6].

In Nigeria, the food processing sector is important at the national level, given the number of companies and industrial production. The sector is very active and provides essential services in the supply of various consumer products in major urban centres. They discharge their wastes into the water body in the process of production. These effluents come from a diversified food processing sector such as brewing, dairy and sugar industries, distilleries, oil mills and sweet manufacturing.

Whenever industrial wastewater is discharged into a body of surface water, care must be taken to avoid damaging any sensitive ecosystem and to ensure that no long-term accumulation of pollutants occurs in the sediments and that the overall use of water in question is not impaired. Untreated or incompletely treated effluents contain algae materials, non-biodegradable organic matter, heavy metals, and other toxicants that deteriorate the receiving stream. Biodegradable pollutants constitute those that can be broken down by micro-organisms and hence their effects are short-lived in the environment. Problems set in when inputs into the environment exceed the environmental capacity to decompose. Some of these biodegradable pollutants include fertilisers, organic compounds that affect the pH, temperature, turbidity, salinity COD, BOD etc. Non-biodegradable pollutants are those that cannot be broken down by micro-organisms and can persist in the environment and become toxic. Examples of these pollutants include heavy metals, PAHs, HCFC, DOT, CFC etc.

Metallic elements are environmentally ubiquitous, readily dissolved in and transported by water, and readily taken up by aquatic organisms. Heavy or toxic metals are trace metals that are at least five times denser than water. They generally do not break down further into less harmful constituents; and accumulate where they are released. As such, they are stable (cannot be metabolized by the body) and bio-accumulative. They are sometimes passed up the food chain to humans. Some metals are essential to biota but could be very harmful when present in excessive concentration. Heavy metals are non-degradable and very harmful to plants, aquatic organisms, and human health at a certain level of exposure [7].

Polycyclic aromatic hydrocarbons are organic pollutants and composed of two or more fused aromatic rings of carbon and hydrogen atoms, which are primarily colourless, white, or pale-yellow solid compounds due to their inherent properties, PAHs are persistent pollutants having a wide range of biological toxicity; remediation of PAHs from the environment has been a global concern. The PAH pollutants are ubiquitous, found equally in aquatic and terrestrial ecosystems as well as in the atmosphere [8]. The United States Environmental Protection Agency (USEPA) has declared 16 PAHs as priority pollutants in 1983 based on their existence of highest concentrations, greater exposure, recalcitrant nature, and toxicity [9-10]. PAHs are characterized by their low water solubility, low vapour pressure, and high melting and boiling points, depending on their structures [11]. PAHs with increased molecular weight are tending to decrease water solubility and increase lipophilicity, making them more recalcitrant compounds [12].

Statement of the Problem

The uncontrolled release of effluents poses undesirable health effects to man and his ecosystem at large, as they may contain a toxic number of heavy metals such as cadmium, chromium, iron etc.

Organic contaminants such as PAHs and n-Alkanes which are hazardous to man and aquatic systems could also be noticeable in these effluents.



The study was therefore imperative to ascertain the presence or absence of these toxic substances in the effluent of the food industry.

Aim and Objectives of the Study

The aim of the study was to determine the physicochemical constituents, heavy metals and organic contaminants concentrations in effluent from a Food processing industry.

Specifically, the study was guided by the following objectives:

1. To determine the levels of the physiochemical parameters in the effluent sample of the food industry
2. To determine the concentration of heavy metal cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn..) in the effluent of flour milling industries.
3. To determine the presence of Poly Aromatic Hydrocarbons and n-Alkanes in effluent sample of the food industry.

Significance of the Study

1. This study is significant as it provided useful information on concentration of heavy metals and organic contaminants present in effluents from food industries.
2. The result obtained will help relevant agencies to establish a monitoring programme to ensure effluent are treated before being discharged into the environment,
3. The research will help relevant regulatory agencies to put in place proactive measures on sensitizing the facility on the need to use the best available technology in treating their effluent prior to discharge.
4. The study will add to existing knowledge as data obtained would be used as a reference for further studies.

Materials and Method

Study Area

Port Harcourt is the capital and largest city of Rivers_State, Nigeria. It is one of the largest city in Nigeria and lies along the Bonny_River and is located in the Niger_Delta. As of 2016, the Port Harcourt urban_area has an estimated population of 1,865,000 inhabitants, up from 1,382,592 as of 2006.

Abonnema, originally known as **Nyemoni** (which means "covet your own" in the Kalabari dialect of the Ijaw language), is a large town in the Kalabari Kingdom that was founded in 1882. Its territory was discovered by an expedition of eleven independent chieftaincy houses from the Kalabari city-state (Elem Kalabari).

The Abonema Wharf River receives effluent discharges from flour milling /processing industries and various mini-factories whose effluents are discharged into the river through drains and Waterways during the rainy season. The industry was chosen for the study based on effluent characteristics.

Material and Reagents

Material

2.5L pre- cleaned Winchester bottle, BOD bottle, Hand trowel, Aluminum foil and Polyethylene bag

The reagents used for the study were; Dichloromethane DCM, N-Hexane, Acetone, Silica gel 60-120 mesh, Anhydrous sodium sulphate, Manganese sulphate, Nitric acid HNO₃, Hydrochloric acid HCl, Perchloric acid HClO₄, Hydrogen tetraoxosulphate (VI) acid H₂SO₄, Ammonium pyrrolidine dithiocarbamate APDC, Methyl isobutyl ketone MIBK, Nitrate Pillow and Sulphate Pillow

The Equipment used for the study were;

PH Hand held Electronic meter; Hannah DI-4337, Hand held Electronic Conductivity meter HI-4103, Hand held Electronic TDS meter D4-7103, Oxygen Meter, BOD Meter, COD Meter, Atomic absorption Spectrophotometer and Agilent Gas Chromatography, FID.

Sample Collection and Preparation

Triplicate effluent samples were collected randomly from the sample site for 3 different days between 14-17 April, 2021 in a 1L plastic bottle. The effluent samples were acidified to pH 1.5 with nitric acid after collection. The acidified samples were kept in an ice chest for preservation and transported to the laboratory.



Methods for the Physical Analysis of water samples

Determination of pH

Method: pH was measured by Electrometric Method using Laboratory pH Meter Hanna model HI991300 [13].

Procedure

- i) The electrodes were rinsed with distilled water and blot dry.
- ii) The pH electrodes was then rinsed in a small beaker with a portion of the sample.
- iii) Sufficient amount of 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 adjusted accordingly.
- v) The pH meter was turn on and the pH of sample recorded

Determination of electrical conductivity

Method: Analysis was carried out according to APHA 2510 B guideline Model DDS-307 [13]

Procedures

- A) The conductivity cell was rinsed with at least three portions of the sample.
- B) The temperature of the sample was then adjusted to $20 \pm 0.1^\circ\text{C}$.
- C) The conductivity cell containing the electrodes was immersed in sufficient volume of the sample
- D) The Conductivity meter was turned on and the conductivity of the sample recorded.

Determination of total dissolved solids

Method: Total dissolved solid was determined using APHA 2510 A TDS 139 tester [13]

Procedures

- i) 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. Continuous suction was then applied to remove all traces of water.
- ii) A clean evaporating dish was heated to $180 \pm 2^\circ\text{C}$ in an oven for 1hr, Cooled and stored in a desiccator until needed. It was usually Weighed immediately before use.
- iii) A sample volume was chosen to yield between 2.5 and 200mg dried residue.
- iv) 50ml of well mixed sample was filtered through the glass-fibre filter; it was washed with three successive 10ml volumes of distilled water, allowing complete draining between washings. Suction was continually applied for about 3mins after filtration is complete.
- v) Filtrate was transferred to a weighed evaporating dish and evaporated to dryness on a steam bath.
- vi) The evaporating dish was finally dried for at least 1hr in an oven at $180 \pm 2^\circ\text{C}$, cooled in a desiccator to balance temperature and weigh.

Calculation:

$$\text{TDS} = \frac{(A - B) \times 10^3 \text{ mg/l}}{\text{Sample volume in ml}}$$

Sample volume in ml

Where A = weight of dish + solids (mg)

B = weight of dish before use (mg)

Determination of total solids

Total solids was the term applied to the material residue left in the vessel after evaporation of the water sample and its subsequent drying in an oven at a temperature of 103-105°C. Total solids include Total Suspended Solids and Total Dissolved Solids [13].

Procedure

100ml of the water samples (50ml) was measured into a pre-weighed dish and evaporated to dryness at 103°C on a steam bath. The evaporated sample was dried in an oven for about an hour at 103-105°C, cooled in a desiccator and recorded for constant weight.



Determination of total suspended solids

Total suspended solid was determined by subtracting the result of total dissolved solids from total solid.

Total solids (TS) – Total dissolved solids (TDS) = Total Suspended solids (TSS) [13]

Methods for the chemical analysis of water samples

Determination of water hardness: 50cm³ of the water sample was introduced into a beaker and 1cm³ buffer solution of NH₃ added. Three drops of solochrome Black T indicator were also added and the solution swirled properly. The mixture was titrated with 0.01EDTA solution until the colour changed from wine red to pure blue with no bluish tinge remaining. The total hardness of the water sample was calculated.

$$\text{Total hardness (mg/cacO}_3) = \frac{\text{Volume of Titrate} \times 1000}{\text{Volume of samples (cm}^3)}$$

Nitrate Determination

Method: Nitrate is determined using PD303 UV Spectrophotometer [13].

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 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 disulfonic acid added and diluted to 500ml, to give 1ml = 10 µg. The solution of various strengths ranging from 0.0 (blank) to 1.0 mg/L at the intervals of 0.2 mg/L was prepared by diluting stock solution with distilled water.

Phosphate determination

Methods: Phosphate was measured using Standard Method 4500-P B.5 and 4500-PE [13]

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 pipette into another conical flask. 1ml of 18M H₂SO₄ and 0.89g of ammonium persulphate were added to both conical flasks and gently boiled for 1 ½ hrs, keeping the volume of 25-50cm³ with distilled water.

It was then cooled, one drop of phenolphthalein indicator was added and after neutralized to a faint pink colour with the 2M NaOH solution. The pink colour was discharged by drop wise addition of 2M HCl, and the solution made up to 100ml with distilled water. For the colorimetric analysis, 20ml of the sample was pipette into test tubes, 10ml of the combined reagent added, shaken, and left to stand for 10mins before reading the absorbance at 690nm on a spectrophotometer, using 20ml of distilled water plus 1ml of the reagent as reference.

Methods for Calibration

Standard phosphate solution: 219.5 mg of dried AR potassium hydrogen phosphate was dissolved in distilled water and made up to 1000ml, where 1ml = 50.0 µg. Of phosphate. 10ml of the stock solution was made up to 1000ml to give 1ml = 0.05 mg. 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.

Sulphate determination

Method: sulphate analysed according to APHA standard method [13]



Procedure

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

The dish was rinsed, and the filter paper washed with several portions of distilled water and both filtrate and washings 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 30minutes, filtered and the filter paper washed with warm distilled water. It was then ignited, cooled and weighed in an already weighed crucible.

Calculation.

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

Biological Oxygen Demand Determination

The general equation for the determination of a BOD value is:

$$\text{BOD (mg/l)} = D_1 - D_5$$

Where D_1 = initial DO of the sample, D_2 = final DO of the sample after 5 days, and P = decimal volumetric fraction of sample used.

If 100 ml of sample are diluted to 300ml, then $P = 0.33$. Notice that if no dilution was necessary, $P = 1.0$ and the BOD is determined by $D_1 - D_2$.

Chemical Oxygen Demand Determination

Introduce 10.0cm³ of the water sample into 100cm³ round- bottom flask, and add 2cm³ 0.1M potassium dichromate, 2.5cm³ 0.01M mercuric sulphate solution, 10ml concentrated sulphuric acid containing silver sulphate, and an anti – bumping rod [13].

Heat to gentle, but steady boiling over an electric hot plate or heating mantle and under a reflux condenser. After exactly 45 minutes boiling, allow to cool briefly, wash 20cm³ distilled water through the condenser into the flask and cool completely in cold water. Add 2 drops of ferroin solution and titrate the excess potassium dichromate with ammonium iron (II) sulphate until the colour changes from bluish- green to reddish brown

Determine a blank with 10.0cm³ distilled water under the same conditions.

Standardization of ammonium iron (II) sulphate.

Dissolved Oxygen in Water determination

Carefully remove the stopper from the sample bottle and add in turn 1cm³ manganous sulphate solution followed by 1cm³ alkaline – iodide – azide solution. When introducing various reagents into the full bottle of sample, the tips of the pipettes should be well below the surface of the liquid. Replace the stopper carefully after each addition to avoid inclusion of air bubbles. Thoroughly mix the contents by inversion and rotation until a clear supernatant water is obtained.

Add 1cm³ concentrated sulphuric acid with the tip of the pipette below the level of solution and again replace the stopper. Mix well by rotation until the precipitation has completely dissolved. Pipette into a 250cm³ conical flask 100cm³ of the solution and immediately titrate it against standard sodium thiosulphate (0.0125 mol dm³) using freshly prepared starch solution as the indicator (add when solution becomes pale yellow). Carry out the titration in duplicate.

Chloride Determination

Method: Chloride analysed according to APHA standard method (APHA, 2005)

Procedure: A 100ml of the clear sample was pipetted into an Erlenmeyer flask and then 1ml of K₂CrO₄ indicator solution was added and titrated with 0.01M standard solution of AgNO₃ in a permanent reddish brown colouration. The AgNO₃ titrant was standardized and a reagent blank established. A blank of 0.2-0.3ml is usual for the method

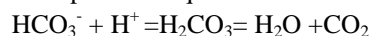
Calculation

Chloride conc = Titre value (x) x 10 = 10xmg/l



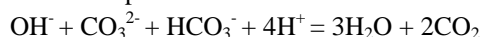
Total Alkalinity

Add two drops of mixed indicator into the sample (solution) in which phenolphthalein alkalinity were determined. Titrate with 0.02M standard HCl until, at pH 4.6, the colour changes pink for mixed indicator or a change from yellow colour to orange for methyl orange indicator. The conversion obtained in this step corresponds to equation:



Total alkalinity as Mg/l $\text{CaCO}_3 = \frac{VT \times M \times 100,000}{\text{mL of sample}}$

mL of sample.



Bicarbonate of Water Sample

Titration Method

This was determined by titration method 50mL or 100mL of the water sample was collected in a clean flask and slight excess of Barium Chloride solution was added to precipitate the carbonate which does not affect the bicarbonate. Two (2) drops of phenolphthalein indicator was added to the solution. It was then shake and titrated to the end point with 0.02M standard HCL (hydrochloric Acid). The volume of acid used was recorded and this calculation as:

$\frac{V \times M \times 100,000}{\text{mL of sample used}}$

mL of sample used

Methods for the elemental metal analysis

metal analysis was conducted using Varian AA240 Atomic Absorption Spectrophotometer according to the method of APHA 1995 (American Public Health Association) [14].

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

Preparation of Samples for GC Analysis [15]

Soxhlet Extraction Method

1. Twenty grams (20g) of the homogenized sample
2. Mix with 60g of anhydrous sodium sulphate in agate mortar to absorb moisture.
3. Place homogenate into a 500ml beaker
4. Carry out extraction with 300ml of n – hexane 24h.
5. Crude extract obtained is evaporated using a rotary vacuum evaporator at 40⁰c, just to dryness.
6. Residue transferred with n – hexane onto a 5ml florasil column for clean up.

Florasil Clean Up

1. Florasil is heated in an oven at 130⁰c overnight (ca.15h) and transferred to a 250ml size beaker and placed in a desiccator.



2. A 0.5g anhydrous Na₂SO₄ was added to 1.0g of activated flosiril (magnesium silicate) (60 – 100nm mesh) on an 8ml column plugged with glass wool.
3. Packed column filled with 5ml n – hexane for conditioning. Open stopcock to allow n – hexane run out until it just reaches top of sodium sulphate into a receiving vessel whilst tapping gently the top of the column till the florisol settled well in the column.
4. Transfer extract on to the column with disposable Pasteur pipette from an evaporating flask
5. Rinse each evaporating flask twice with 1ml portions of n – hexane and add to column.
6. Eluate collected into an evaporating flask and rotary evaporated to dryness.
7. Dry eluate dissolved in 1ml n – hexane for PAH Chromatographic analysis.

Fixed Setting

Generally the operator must adjust gas flows to the columns, the inlets, the detectors, and the split ratio. In addition, the injector and detector temperatures must be set. The detectors are generally held at the high end of the oven temperature range to minimize the risk of analyte precipitation. All of these parameters should have been set to the correct values, but double check all the instrument: Buck 530 gas chromatograph equipped with an on – column, automatic injector, Mass spectroscopy, HP 88 capillary column (100m x 0.25µm film thickness,) CA, USA

Detector Temperature A: 250 °C

Injector temperature 22 °C

Integrator chart speed: 2cm/min

Set the OVEN TEMP to 180 °C and allow the GC to warm up. While its warming,

When the instrument is ready, the ‘NOT READY’ light will turn off, and you can begin your Run. Inject a 1 microliter sample onto column A using proper injection technique.

Preparation of Samples for GC Analysis TPH [15]

Soxhlet Extraction Method

1. Ten grams (10g) of the homogenized sample
2. Mix with 20g of anhydrous sodium sulphate in mortar to absorb moisture.
3. Place homogenate into a 500ml beaker
4. Carry out extraction with 300ml of n – hexane 24h.
5. Crude extract obtained evaporated using a rotary vacuum evaporator at 40⁰c, just to dryness.

Preparation of sample for GC analysis

Dissolve 1ml of filtered residue in 50ml of chloroform and transferred to a 100ml volumetric flask and dilute to the mark. Evaporate most of the chloroform at room temperature Next, add 1 ml of the reagent {20 vol% benzene and 55 vol% methanol}. Seal it and heat it at 40⁰c water bath for 30 minutes. After heating, extract the organic sample with hexane and water,so that the final mixture of the reagent, hexane and water, is in proportion of 1:1:1 (i.e., add 1ml each of hexane and water to the reaction mixture). Shake the mixture vigorously by hand for 2min. if a stable emulsion is formed, break it by centrifugation. Transfer about half of the top hexane phase to a small test tube for injection. Be careful to remove only the organic layer. Do not inject directly from the reaction vial because of the risk of injecting water. Water can ruin the GC column. `

Fixed Setting: Generally, the operator must adjust gas flows to the columns, the inlets, the detectors, and the split ratio. In addition, the injector and detector temperatures must be set. The detectors are generally held at the high end of the oven temperature range to minimize the risk of analyte precipitation. All these parameters should have been set to the correct values, but double check all the instrument: Buck 530 gas chromatograph equipped with an on – column, automatic injector, Electron capture detector, HP 88 capillary column (100m x 0.25µm film thickness,) CA, USA

Detector Temperature A: 280 °C

Column temperature 210 °C

Injector temperature 250 °C



Integrator chart speed: 2cm/min

Set the OVEN TEMP to 180 °C and allow the GC to warm up.

When the instrument is ready, the ‘NOT READY’ light will turn off, and you can begin your

Run. Inject a 1 microliter sample onto column A using proper injection technique.

Preparation of standard

10ul of accurate standard was injected in the chromatography and the retention time compared with retention time of standard.

Results and Discussions

The result of the physicochemical parameters is presented in Table 1 and shown graphically in Figure 1

The result of the heavy metals analysis was presented in Table 2, and represented graphically using a bar chart as shown in Figure 2

The PAHs analysis result was presented in Table 3-5, and represented graphically in Figure 3

The n-Alkanes analysis result was presented in Table 6, and shown graphically using bar chart in Figure 4

Table 1: Levels of Physiochemical Parameters in Effluent Samples

Physicochemical parameters	Sample 1	Sample 2	Sample 3	Mean±S.D	WHO Standard
Chloride (Cl ⁻)(mg/l)	97.98	97.00	97.02	98.00±1.01	250
Total Hardness(mg/l)	102	106	104	104.00±2.0	-
Nitrate (NO ₃ ⁻)(mg/l)	5.942	5.943	5.929	5.94±0.008	4.0
Phosphate(mg/l)	4.336	4.329	4.331	4.332±0.003	3.5
Dissolved Oxygen(mg/l)	44.34	44.38	44.39	44.37±0.026	3.0
Turbidity(NTU)	7.39	7.49	7.41	7.43±0.053	5.0
Electrical conductivity (µS/cm)	106.28	106.37	106.34	106.33±0.046	1000.00
Total Dissolved Solids(mg/l)	122.46	122.35	122.48	122.48±0.07	50.00
Sulphate (SO ₄ ²⁻)	87.35	87.30	87.37	87.37±0.036	200.00
TS (mg/l)	146.31	146.30	146.35	146.35±0.026	500.00
pH	5.94	5.99	6.00	5.98±0.036	6.0-8.5

Table 2: Concentration in mg/l of Metals in effluent Samples

Metal	Sample 1	Sample 2	Sample 3	Mean ± S.D	WHO Standard
Na	1.439	1.456	1.458	1.451± 0.01	75.0
K	0.082	0.075	0.077	0.078±0.036	-
Mn	0.078	0.072	0.062	0.070 ±0.008	0.10
Fe	0.014	0.013	0.015	0.014 ±0.001	0.30
Cu	0.189	0.196	0.197	0.194±0.004	2.0
Cr	0.014	0.012	0.013	0.013± 0.001	0.05
Cd	0.485	0.494	0.491	0.490± 0.003	0.003
Zn	0.178	0.188	0.174	0.180±0.007	1.0

Table 3: Concentration of carcinogenic PAHs in effluent sample

PAHs	Sample 1	Sample 2	Sample 3	Mean ± S.D
Flourene	0.481	0.474	0.464	0.473± 0.009
Dibenzyl(a,h)anthracene	11.798	11.890	11.991	11.893±0.10
Anthracene	13.998	13.993	13.997	13.996±0.003
1,2 Benzanthracene	15.230	15.226	15.213	15.223±0.009
Benzo(k)floranthrene	17.186	17.179	17.184	17.183±0.004
Benzo(a)pyrene	25.318	25.324	25.318	25.320±0.003
pyrene	34.377	34.371	34.371	34.373±0.003
Benzo(g,h,i)pyrene	38.293	38.288	38.389	38.290±0.006
Benzo(b) Flouranthrene	39.98	41.06	41.24	40.76±0.002



Table 4: Molecular diagnostic ratios and possible sources of PAHs in the effluent samples

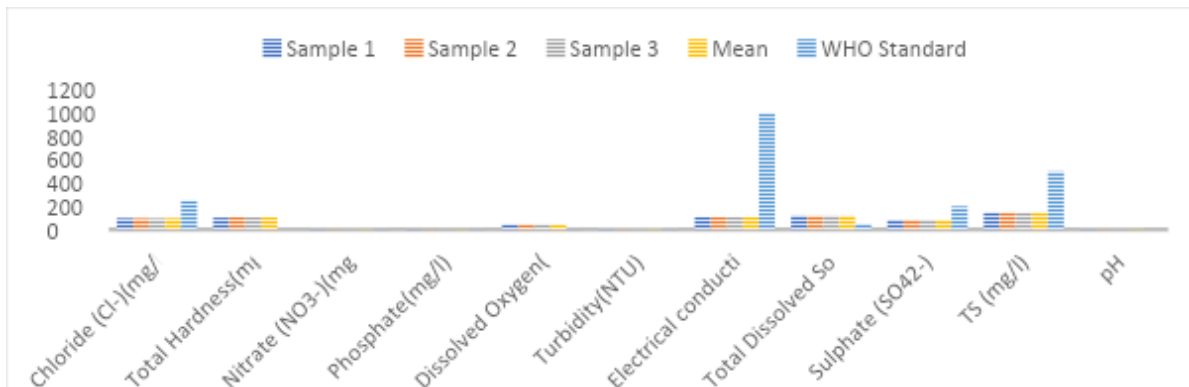
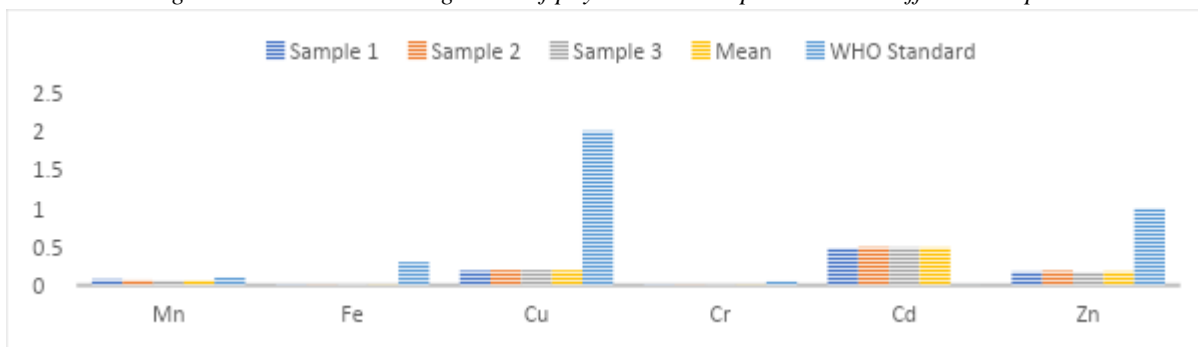
LMW/HMW	Fl/(Fl+Pyr)	BbF/BkF	BaP/(BghiA)
0.079	0.018	2.34	0.66

Table 5: Ring size of PAHs in the effluent samples in mg/l

2-3	4	5	6
14.419	49.575	94.656	38.29

Table 6: Concentration in mg/l of n-alkanes in Effluent Samples

n- alkanes	Sample 1	Sample 2	Sample 3	Mean±S.D
Hexane (C6)	0.039	0.32	0.037	0.036±0.004
Octane (C8)	1.127	1.30	1.121	1.126±0.005
Nonane (C9)	3.370	3.385	3.373	3.376±0.008
Decane (C10)	3.398	3.794	3.799	3.797±0.003
Dodecane (C12)	7.859	7.855	7.845	7.853±0.007
Tridecane (C13)	9.789	9.798	9.792	9.793±0.005
Heptadecane (C17)	13.019	13.011	13.018	13.016±0.004
Octadecane (C18)	19.052	19.048	19.094	19.05±0.003
Nonadecane (C19)	19.609	19.604	19.605	19.606±0.003
Tetracosane (C24)	22.735	22.737	22.718	22.73±0.005
Hexacosane (C26)	26.117	26.115	26.114	26.115±0.002
Dotriacontane (C32)	28.693	28.698	28.697	28.696±0.003
Hexatriacontane (C36)	1.127	42.228	42.235	42.233±0.004

**Figure 1:** Bar chart showing levels of physicochemical parameters in effluent sample**Figure 2:** Bar chart showing concentration (mg/l) of Heavy metals in effluent samples

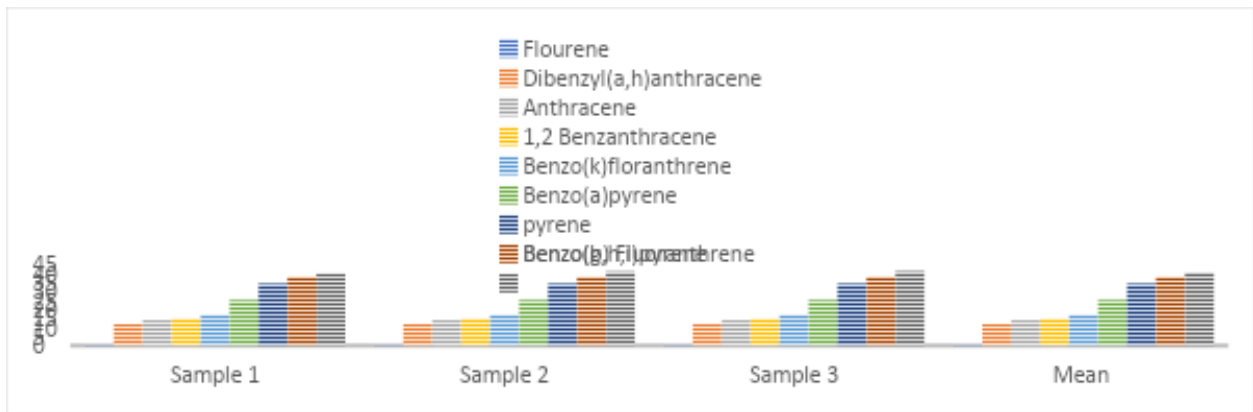


Figure 3: Bar chart of concentration (mg/l) of PAHs in effluent samples

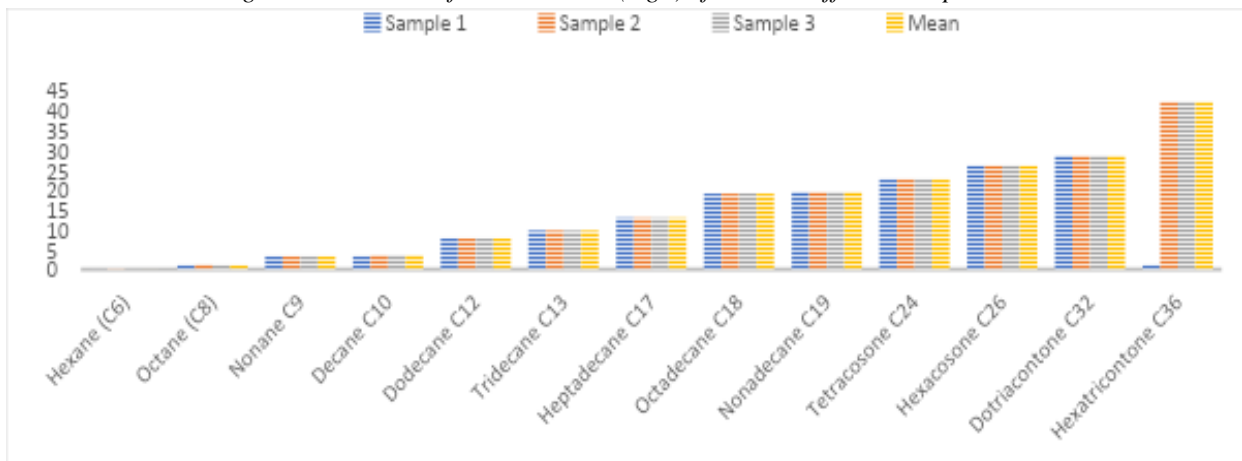


Figure 4: Bar chart of concentration (mg/l) of n-alkanes in effluent samples

Discussion

The result of the physicochemical parameters showed that the levels of Nitrate, Phosphate and Dissolved Oxygen were above the World Health Organisation standard for effluent while the others were below. Below is a brief discussion on each of the parameters.

The value obtained for turbidity in the effluent sample was 7.43 ± 0.053 NTU and was higher than the World Health Organisation standard value of 5 NTU for discharge of wastewater into the stream. The value obtained from the study was below the 30.40-34.30 NTU obtained from a similar study carried out by Jingxi et al., [16] in the determination of physicochemical parameters and heavy metals in food wastewater. High turbid waters are often associated with the possibility of microbiological contamination as high turbidity makes it difficult to disinfect water properly.

The pH of the sample is 5.98 ± 0.036 as presented in Table 3. The value obtained is slightly lower than the World Health Organisation set limit of 6-8.5 and lower than the value of 7.21 gotten from a study on the effect of food processing industries effluent on the environment by Amabye, [17]. The value obtained from the study was lower than the pH range of 6-8 reported by Echiegbu and Liberty, [6] in the determination of effluents characteristics of some selected food processing industries in Enugu and Anambra state. The ideal range of pH for aquatic growth is 6.8 to 9.0. pH greatly affects biological activity. It also affects some properties of the water body, activity of organisms and effects of toxic substances present in the aquatic environment. A high amount of organic matter and pH of 6.9 to 8.6 keeps most trace elements immobilized [18].

Total Hardness is the total calcium and magnesium ion concentration in the water sample and to a lesser extent, iron, and manganese. The water of medium hardness is desirable for steamed bread production as some of the mineral salts have a strengthening effect on gluten and stimulate yeast. Industrial processing can also introduce ions that can cause hardness in the effluent which are subsequently discharged into the water body. From table



3, the value of hardness in the water sample is $104 \pm 2.0 \text{ mg/l}$ which is consistent with the mean value of $100 \pm 2.89 \text{ mg/l}$ reported for FAN Milk Company in the study carried out by Adebisi and Feyemiwo, [19]. It was, however, above the 40.0 mg/l reported by Amabye, [17] in his investigation of the effect of food processing effluents on the environment.

The electrical conductivity of water is a useful indicator of its salinity or total salt in a water/effluent sample. The mean value of EC was $106.33 \pm 0.046 \mu\text{s/cm}$ as shown in Table 3. The mean conductivity value for the sample was below the WHO guideline values of 1000 s/cm for the discharge of wastewater through the channel into the stream. The value gotten from the study is higher than the values obtained by Adebisi and Feyemiwo [19] in their work on the effluents of two Industries. They had a value of $14 \mu\text{s/cm}$ for Fan Milk company and $17.0 \mu\text{s/cm}$ for Agro Oil. However, the value is below $1321.3\text{-}4465.1 \text{ mg/l}$ obtained by Nazish and Jaitly, [20] in their study of metal ions, physicochemical parameters from industrial effluent of Bareilly.

Total Suspended Solids are a direct indication of the solids removable by sedimentation and also an index of the sludge forming characteristics. The value obtained from the study was $146.32 \pm 0.026 \text{ mg/l}$ (Table 3) which exceeds the WHO permissible limit of 30.0 mg/l . The value is higher than 21.15 for station 1 and 30.05 mg/l for station 2 obtained from another study on effluents in part of Edo state by Ewere et al., [21]. This was also higher than the value of 0.53 mg/l reported for the Nigerian Bottling Company plant in Maiduguri, Nigeria by Arku, et al., [22]. Suspended solids may kill fish and other aquatic fauna by causing abrasive injuries by clogging the gills and respiratory passages, by blanketing the stream bottom, destroying the spawning beds, and screening out light necessary for the photosynthetic activity of aquatic plants.

The TDS value of the sample is 122.43 mg/l (Table 3). The value obtained was above the WHO standard of 50.0 mg/l and higher than the value of $34.3 \pm 0.34 \text{ mg/l}$ in the study carried out by Akaninwor et al, [23] on levels of heavy metals and physicochemical parameters of effluents from a Beverage company in Rivers State. This was also below the value of $166.73\text{-}6017.67 \text{ mg/l}$ gotten from the evaluation of physicochemical parameters and some heavy metals from Tannery effluents of Sharada and Challawa Industrial Area [24]. Higher TDS can be toxic to aquatic life by changing the composition of the water [25].

From Table 2, the dissolved oxygen in the effluent sample is 44.37 mg/l which is higher than the value of 17.41 mg/l obtained by Adebisi and Fayemiwo, [19] in their study of the physicochemical properties of Industrial Effluent in Ibadan. The value was however lower than 2.86 and 1.12 mg/l obtained from two industries in Agbara, Lagos [26].

Conclusion

Based on the result of this research, it was observed that the physicochemical levels of physicochemical parameters such as phosphates, nitrates and dissolved oxygen were below the recommended limit set by World Health Organisation for effluents. The levels of metals were in the order $\text{Na} > \text{Cd} > \text{Cu} > \text{Zn} > \text{K} > \text{Mn} > \text{Fe} > \text{Cr}$ with the concentration of cadmium above the World Health Organisation set limit. The effluent had organic contaminants such as Poly Aromatic Hydrocarbons (PAHs) and n-alkanes. The

Recommendations

Based on the findings from this research work, it is recommended that:

1. The FEPA guidelines should be reviewed to include effluent and other limitations for such specific industries like breweries, vegetable oil and other food processing industries not already covered by the guidelines. Also limitations for many other relevant pollution parameters should be included.
2. Federal and the State Environmental Protection Agencies should carry out routine checks on industries especially food processing industries with a view to ensuring compliance
3. Awareness should be created among the industrialists, workers, and the inhabitants on the need to be environmental friendly.
4. The national Environmental Quality Standards (NEQS) regarding wastewater should be strictly enforced on these industries to install wastewater treatment plants.



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