

Comparative Study of the Physicochemical and Heavy Metals Parameters of Some Selected Processing Industries Effluents in Port Harcourt Metropolis, Nigeria

Evbuomwan B.O and Osia O. G

Department of Chemical Engineering, University of Port Harcourt, Port Harcourt, Nigeria

Abstract—The physicochemical and heavy metals parameters of some selected processing industries effluents in Port Harcourt Metropolis, Nigeria has been investigated. The effluents from Food and Brewery industries were collected and analysed for BOD, COD, TSS, pH, Total bacteria count and heavy metals, using standard methods of analysis. The results obtained after the analysis are: BOD(27.52±7.94 to 43.2 ±12.49),COD(219±63.22 to 263.6±76.12),TSS(100±28.86 to 700 ±202.07),Total bacteria count($4.9 \times 10^4 \pm 1.4 \times 10^4$ to $3.5 \times 10^7 \pm 1.01 \times 10^7$), pH(4.83±1.39 to 7.32 ±2.11),zinc(0.36±0.10 to 16.3±4.70), lead(1.24±0.35 to 2.53±0.73), Iron(151±43.58 to 1160±334.8),cadmium (0.08±0.023 to 0.11±0.03),chromium(0.54±0.155 to 0.58±0.16).These were compared with World Health Organization standard for wastewater. The physicochemical parameters(COD,TSS,total bacteria count) for both industries were above the standard limits set by WHO, but only BOD and pH values for food industry are within the limit. And also the heavy metals for both Industries are above the limits ,except for zinc from food industry,which is below the standard limit.

Keywords— Food, Brewery, Heavy metals, Physicochemical and Effluents

INTRODUCTION

The last two decades marked the emergence, growth and development of food processing industries (both foreign and indigenous) in Nigeria. This is due to increasing demand for processed food, particularly in urban areas. The raw materials for the processed food industries are mainly agricultural, from where finished products such as beverages, edible oils, sugars and other sweeteners, drinks (both alcoholic and non-alcoholic), fish and meat products emerge[1].

Food processing as an industry was introduced into Nigeria by the United African Company (UAC) in 1923. Today, food industries in the country are so many that they can be subdivided into 13 categories, namely: flour and grain; soft drinks and carbonated water; breweries; starch and miscellaneous food products; meat, poultry and fish; tea, coffee and other

beverages; fruit juices; animal feed; sugar; distilleries and blending of spirits; cocoa, chocolates and sugar confectioneries; agricultural and food chemicals; and industrial packaging [2]. Food processing projects involve the processing and packaging of meat products, fish and shell fish, dairy products, fruit and vegetables, grains and beverages production. It includes refinement, preservation, improvement of product; storage, handling, packaging and canning. The processing may involve receiving and storing raw or partially processed plant, animal or other food materials, processing the raw materials into finished products, and packaging and storing the finished products. The processing industries are a part of our environment and are often major generators of wastes. Since the existing environment within which they operate is the only one we have, and shared by both the consumers and operators of other sectors of the economy, there is the need therefore, to ensure the preservation of the environment in as natural and ecologically balanced a state as possible for the use of all. This must and should be made to be the motivating factor during the design, construction and operation of all industrial enterprises. Industrial waste is a major source of environmental pollution that affects the waterbodies of an area. The food industries should be aware of the contents of the wastes they generate with the view to making them environment friendly[1].

Heavy metals, also known as trace metals, are one of the most persistent pollutants in wastewater. The discharge of high amounts of heavy metals into water bodies leads to several environmental and health impacts. The exposure of humans to heavy metals can occur through a variety of routes, which include inhalation as dust or fume, vapourisation and ingestion through food and drink. Some negative impacts of heavy metals to aquatic ecosystems include death of aquatic life, algal blooms, habitat destruction from sedimentation, debris, increased water flow, other short and long term toxicity from chemical contaminants [3].

Wastewater is the primary area of concern at the food and beverage industry. With the exception of some toxic cleaning products, wastewater from food processing facilities is organic and can be treated by

conventional biological technologies [4]. Primary issues associated with food and beverage industrial wastewater are biochemical oxygen demand (BOD); chemical oxygen demand (COD); total suspended solids (TSS); excessive nutrient loading (nitrogen and phosphorus compounds); pH of the water; total alkalinity and pathogenic organisms. Solid wastes from the food and beverage industries include both organic and packaging waste. Organic wastes from raw materials such as food grain, flavoring and coloring agents results from processing operations. Inorganic waste typically includes excessive packaging items like plastic, glass, and metal [5].

Industrial wastewaters are considerably diverse in their nature, toxicity and treatability, and normally require pre-treatment before being discharged to sewer. Food processing in particular is very dissimilar to other types of industrial wastewater, being readily degradable and largely free from toxicity. However, it usually has high concentrations of biological oxygen demand (BOD) and suspended solid [6].

Industrial effluents are discharged into the environment without adequate treatment which contains high concentrations of several organic compounds including carbohydrates, starches, proteins, vitamins and sugars which are accountable for high chemical oxygen demand (COD), high biochemical oxygen demand(BOD) and suspended solids(SS) [7]. Food processing industrial effluents are biodegradable but problems can arise if the wastewater is excessively diluted with washing water or is highly concentrated such as undiluted blood or milk [8]. The aim of this paper is to compare the physicochemical and heavy metals parameters of some selected processing industries effluents in Port Harcourt metropolis, Nigeria.

MATERIALS AND METHODS

Study Area

The two processing industries considered for this study are Food and Brewery Industries which are located in Port Harcourt metropolis, Nigeria.

Port Harcourt is a city in the southern part of Nigeria and is of latitude 4°49'27"N and longitude 7°2'1"E. Port Harcourt features a tropical wet climate with lengthy and heavy rainy seasons and very short dry seasons. Only the months of December and January truly qualifies as dry season months in the city. The harmattan, which climatically influences many cities in West Africa, is less pronounced in Port Harcourt. The average monthly temperatures range between 25°C - 28°C in the city [9].



Figure 1: Map of Port Harcourt metropolis.

Method of Sampling:

Wastewater samples were collected using sterilized plastic containers of 2 litres for each of the effluents. The effluents were collected along the course of the discharge channels from the two Industries. The containers were labelled and the samples were stored in a refrigerator to avoid biological actions until the time of analysis. All chemicals used during the experiment are of analytical grades. The wastewater is characterized by determining the following parameters: BOD, COD, pH, TSS, Total bacterial count using standardized procedures and the heavy metal contents were analysed using the Atomic Absorption Spectrometer (AAS).

Determination of Biochemical Oxygen Demand (BOD)

[10]

Procedure;

The method involves filling the samples to overflowing, in an airtight bottle of the specified size and incubating it at the specified temperature for 5days. Dissolved oxygen (DO) was measured initially and after incubation and the BOD was computed from the difference between initial and final (DO). Because the initial (DO) was determined shortly after the dilutions was added, all oxygen uptake occurring after this measurement was included in the BOD measurement. One Millimeter (1ml) of $MgSO_4$, $CaCl_2$, phosphate buffer, $FeCl_3$ were added to 1L of distilled water. The solution was then agitated thoroughly to saturate the dissolved oxygen. This solution was used to dilute samples. One hundred millimeters (100ml) of the samples were measured into different one Liter flasks and were made up to (1L) mark with the dilution

solution previously prepared. The dilution sample solution was then poured into BOD bottles and subsequently incubated at 20°C in the dark for 5 days.

Determination of initial dissolved oxygen:

Three hundred millimeters (300ml) BOD bottles were filled with the diluted samples previously prepared and the initial dissolved oxygen (DO) was determined using the Winkler's method

Determination of Final Dissolved Oxygen: After incubation for 5 days, the final dissolved oxygen (DO)

was determined using the same procedure above.

$$\text{BOD (mg/L)} = [\text{DO}_1 - \text{DO}_0] / B$$

Where DO_0 = initial dissolved oxygen (immediately after preparation)

DO_1 = final dissolved oxygen (after 5 days of incubation)

B = Fraction of sample used.

Determination of Chemical Oxygen Demand (COD).

[10]

Procedure;

250ml of borehole water was warmed to 27°C and transferred to a clean flask. 10ml of KMnO_4 0.0125M was added and 10ml of 20% H_2SO_4 was added. It was mixed gently and incubated at 27°C for 4 hours. The mixture was examined at intervals, when the pink colour of permanganate tends to disappear, 10ml of KMnO_4 was added. After 4 hours, 1ml KI solution was added and titrated with 0.0125M $\text{Na}_2\text{S}_2\text{O}_3$ using starch as an indicator, until the blue colour just disappeared.

Calculation: COD (mg/l) = [(ml of Blank-ml required of sample) x 1000] / A x Volume of sample used.

Where A = Total Volume of KMnO_4 0.0125M added to samples.

Determination of P^H:

The pH was measured by laboratory pH meter, Hanna model H1991300 [11]

Procedure;

100ml of each of the samples were measured and filtered into beakers. The pH meter was turned on and the pH of the first sample was recorded. After the first run, The pH meter electrodes were standardized using a distilled water before taking reading of the second sample.

Determination of Total Suspended Solid:

Gravimetric analysis was used to determine TSS.

Procedure;

100ml of each of the effluents were measured out into a beaker. Whatman filter paper was used for the filtration process. The initial weight of the filter paper

was noted as it was oven dried for 5 minutes 100ml of the sample was then filtered. After filtration, it was the oven dried at 105°C to get the Total solids, then it was weighed and recorded. The same filter paper was also oven dried for 550°C to get the total suspended solid (non volatile solids) and it was the weighed and recorded.

Calculation;

$$\text{TSS} = \frac{(\text{final weight of filter} - \text{initial weight of filter}) \times 1000}{\text{Sample volume (L)}}$$

Total Bacterial Count.

Standard Plate Count method was used in determining total bacteria count.

Principle:

Nutrient agar is a general purpose growth medium commonly used to assess "Total" or Viable bacterial growth of a water sample. The number of microorganisms per milliliter of sample is calculated from the number of colonies obtained on Nutrient agar (NA) plate from selected dilution. Poured plates are prepared using a specified culture medium and a specified quantity of the sample. The plates are incubated at 37°C for 48 hours.

- **Culture Media:**

Nutrient agar

Procedure:

Disinfect the surface of the bottle containing sample with 70% ethanol. Thoroughly mix the sample by vigorous shaking to achieve uniform distribution. Aseptically inoculate 1mL of sample or other suitable dilution of the water sample using sterile pipette into sterile petri plates in duplicate. The petri dishes were labeled with sample numbers and date.

Pour into each plate 15–18 mL of the molten sterilized Nutrient agar (cooled to

44–47°C). Avoid pouring of molten medium directly into the inoculum. Mix the media and inoculum by swirling gently clockwise and anti-clockwise so as to obtain homogenous distribution of inoculum in the medium. Allow to cool and solidify. After complete solidification, invert the prepared petri dish plates and incubate at 37°C for 48 hours.

After specified incubation period, all colonies were counted including pinpoint colonies using colony counter. Spreading colonies shall be considered as single colony. Less than one quarter of petri dish was overgrown by spreading, count the colonies on the unaffected part of the petri dish plate and calculate corresponding number of the entire petri dish plate. If more than one quarter is overgrown by spreading colonies discard the plate.

Heavy Metals Analysis

About 40ml of each of the effluents were measured and a total volume of 100ml of HNO_3 , H_2O_2 , and

H₂SO₄ in the ratio of 40%:40%:20% respectively were mixed together. The samples were then agitated using an electronic magnetic stirrer. Samples were stirred for 5 minutes at a speed of 180rpm Samples were allowed for a contact time of 6 hours, after which the digest was filtered using a Whatman filter paper. Samples were then analyzed using atomic absorption spectroscopy (AAS) model: 210VGF.

Data analysis

Statistical analysis using one way analysis of variance (ANOVA). Mean, variance and standard error were used to assess the spread of the data. Differences in mean values obtained were considered significant if calculated P-values were < 0.05.

RESULTS AND DISCUSSION

Table1: Physicochemical parameters of Food and Brewery effluents

Parameters	Symbol	Food Effluent	Brewery Effluent	P-value	Decision	WHO standard
pH	-	7.32 ±2.11	4.83±1.39	0.382>0.05	Not significant	6.0-9.0
Total bacteria count	Cfu/100ml	4.9×10 ⁴ ±1.4×10 ⁴	3.5×10 ⁷ ±1.01×10 ⁷	0.026<0.05	Significant	400
Total suspended solids	Mg/l	100±28.86	700 ±202.07	0.042<0.05	Significant	30.00
BOD	Mg/l	27.52±7.94	43.2 ±12.49	0.347>0.05	Not significant	30.00
COD	Mg/l	219±63.22	263.6±76.12	0.675>0.05	Not significant	200

Table 2: Heavy Metals Effluents Parameters (Food and Brewery)

Parameter	Symbol	Food Effluent	Brewery Effluent	P-value	Decision	WHO Standard
Zinc	Ppm	0.36±0.10	16.3±4.70	0.028<0.05	Significant	1.00
Lead	Ppm	1.24±0.35	2.53±0.73	0.187>0.05	Not significant	0.10
Iron	Ppm	1160±334.8	151±43.58	0.040<0.05	Significant	0.30
Cadmium	ppm	0.11±0.03	0.08±0.023	0.44>0.05	Not significant	0.003
Chromium	Ppm	0.54±0.155	0.58±0.16	0.870>0.05	Not significant	0.05

Table 3: Physicochemical statistical analysis

	N	Mean	Std. Deviation	Std. Error	Significance	
Ph	EFFLUENT (FOOD)	3	7.3200	3.66000	2.11310	.382
	EFFLUENT (BREWERY)	3	4.8333	2.41500	1.39430	
TBC	Total	6	6.0767	3.08969	1.26136	.026
	EFFLUENT (FOOD)	3	49000.0000	24500.00000	14145.08160	
	EFFLUENT (BREWERY)	3	3500000.0000	1750000.00000	10103629.71082	
TSS	Total	6	17524500.0000	22112710.38114	9027476.21062	.042
	EFFLUENT (FOOD)	3	100.0000	50.00000	28.86751	
	EFFLUENT (BREWERY)	3	700.0000	350.00000	202.07259	
BOD	Total	6	400.0000	397.49214	162.27549	.347
	EFFLUENT (FOOD)	3	27.5200	13.76000	7.94434	
	EFFLUENT (BREWERY)	3	43.2800	21.64000	12.49386	
COD	Total	6	35.4000	18.37292	7.50071	.675
	EFFLUENT (FOOD)	3	219.0000	109.50000	63.21985	
	EFFLUENT (BREWERY)	3	263.6800	131.84000	76.11786	
	Total	6	241.3400	111.12023	45.36464	

Table 4: Heavy metal statistical analysis

		<i>N</i>	<i>Mean</i>	<i>Std. Deviation</i>	<i>Std. Error</i>	<i>Significance</i>
Zn	EFFLUENT (FOOD)	3	.3600	.18000	.10392	.028
	EFFLUENT (BREWERY)	3	16.3000	8.15000	4.70540	
	Total	6	8.3300	10.13938	4.13938	
Pb	EFFLUENT (FOOD)	3	1.2400	.62000	.35796	.187
	EFFLUENT (BREWERY)	3	2.5333	1.26500	.73035	
	Total	6	1.8867	1.13827	.46470	
Fe	EFFLUENT (FOOD)	3	1160.0000	580.00000	334.86316	.040
	EFFLUENT (BREWERY)	3	151.0000	75.50000	43.58995	
	Total	6	655.5000	665.02962	271.49721	
Cd	EFFLUENT (FOOD)	3	.1133	.05508	.03180	.444
	EFFLUENT (BREWERY)	3	.0800	.04000	.02309	
	Total	6	.0967	.04676	.01909	
Cr	EFFLUENT (FOOD)	3	.5400	.27000	.15588	.870
	EFFLUENT (BREWERY)	3	.5800	.29000	.16743	
	Total	6	.5600	.25156	.10270	

The effluent from food industry indicates a higher pH value (7.32 ± 2.11) than the effluent from Brewery (4.83 ± 1.39). though there is no significant difference in pH between the two effluents at $p=0.382$. The effluent value for food is within the permissible limit range set by [12], 6.0-9.0. Whereas, the effluent value for brewery is lower than the permissible limit. The effluents from the Brewery is very acidic and hence making its continuous discharge harmful to aquatic organisms. This is because, with this level of acidity, the effluents could greatly off-set the pH balances of water bodies, thereby making the waters unsafe for drinking or inhabitable for some aquatic organisms[13].

The brewery effluent shows higher values than food effluent and there was no significant difference in BOD of the two effluents at $p=0.347$. The BOD value of Brewery effluent was higher than the permissible limit, but it is not so high compared to the wastewater effluents of some other manufacturing industries such as 240mg/l at a typical tomato processing industry and 260mg/l from the main sewer of a soap and detergent producing industry[14]. COD value from brewery shows higher values than food effluent (219 ± 63.22)mg/l. But COD from both industries were above the standard limit and there was no significant difference in COD of the effluents at $p=0.675$.

High COD levels mean a greater amount of oxidation of organic material in the sample which will reduce dissolved oxygen level when discharged into river and finally lead to the death of aquatic organisms if it continuous.

The study revealed that the TSS values for food and Brewery effluents are (100 ± 28.86) mg/l and (700 ± 202.07) mg/l respectively which are above the standard limit set by WHO. High TSS will degrade the growth of aquatic life because it prevents sun light to penetrate through to the bottom of the water. The bacteria concentration in the tested samples of food and Brewery industries are ($4.9 \times 10^4 \pm 1.4 \times 10^4$)cfu/100ml and ($3.5 \times 10^7 \pm 1.01 \times 10^7$) cfu/100ml respectively.

This shows that there is a great chance that disease causing organisms are present in the two samples, and when introduced to the river, it will surely cause disease to humans who bathe in this water or drink from it.

It was observed that the value of zinc for brewery (16.3 ± 4.70) ppm is higher than that of food industry (0.36 ± 0.10)ppm, but the value for food industry is below the standard limit set by WHO 1.00ppm. and there is a significant difference in zinc between the effluents at $p=0.028$. The fact that the effluent was obtained from a food producing industry could be responsible for the occurrence of some of zinc at high concentration. This is because food producing industries are known to make use of raw material such as table salt, sodium bicarbonate etc. which may be rich in some of these minerals.

The report from [15], stated that the Human daily requirement for zinc is 15mg for adult and 5mg for children. Though excess amount of zinc on the other hand can cause stomach cramps, nausea, vomiting, central nervous system disorder[16].

There is no significant difference in Lead for the two industries at $p=0.187$.

The high level of lead in the samples can be said to be from the parts of the equipment or machinery used at different stages of production.

A chronic exposure to lead can affect physical growth and can also cause anaemia, kidney damage headache [17]

The high level of iron may be due to corrosion in the wastewater outlets of the two Industries. Due to the fact that the level of iron is high in the effluents, an excessive intake of water containing iron may cause Hemosiderosis, which is an overload of iron in the organs or tissues of the body [18].

A constant exposure to cadmium if disposed to the environment leads to nausea, vomiting, and abdominal pain [19].

A continuous discharge of these effluents to the environment can cause health effects like lung cancer and skin ulcer if one is exposed to it especially chromium (vi) [20].

CONCLUSION

The comparative study of the effect of some selected industries effluents in Port Harcourt metropolis showed that based on pH values alone, the effluents from brewery cannot be discharged into waterbodies. Also, the BOD from the brewery is above set limit so it cannot be discharged into the environment. If discharged, it will have a negative effect on aquatic lives.

The COD, TSS, Total bacterial count and heavy metals were above the recommended limit and will have negative impact on the environment.

REFERENCES

[1] O. Chukwu. "Impacts of food processing industry on some environmental health and safety factors" *Caspian J. Env. Sci.*, Vol. 7 No.1 pp. 37-44, 2009

[2] O.O. Ojo, A.O. Ajayi, and I.I. Anibijuwon, "Antibacterial potency of methanol extracts of lower plants". 2006

[3] B.A Apkor, G.O. Ohiobor and T.D. Olaolu, "Heavy metal pollutants in wastewater effluents: sources, effects and remediation;;, *Advances in Bioscience and Bioengineering*, Vol.2, No. 4, 2014, pp37-43

[4] G.Tchobanoglous, "Wastewater Engineering: Treatment, Disposal, and Reuse", Metcalf and Eddy, Inc., 3rd Ed, McGraw-Hill, NY, 1991

[5] J. Katzel, "Managing nonhazardous solid wastes", *Plant Engineering*; v48, n 11, 1994, p42

[6] N.F.Gray, "Water Technology": An Introduction for Environmental Scientists and Engineers", Oxford, Elsvia Butterworth- Heinemann, 2005

[7] M. Kobya., H. Hiz, E. Senturk., C. Aydiner and E. Demirbas., "Treatment of Potato Chips Manufacturing Wastewater by Electrocoagulation. *Desalination* 190, 2006, 201-211

[8] B.Tylkowski and R. Jastrzab,(2017)."Chapter 4. Smart Capsules for Lead Removal from Industrial Wastewater". In Astrid, S.; Helmut, S.; Sigel, R. K. O. Lead: Its Effect on Environment and Health. *Metal Ions in Life Sciences*. 17. de Gruyter.2017, pp. 61-78.

[9] World Weather Information Service "World Meteorological Organization". Archived from the original on 17 August, 2016

[10] L.W.Winkler, "Die Bestimmung des, A Wasser gelosters Sauesrtoffen *Berichte der Deutschen Chemischen" Gesellschaft*, 21, 1088, 2843 - 2855

[11] APHA, "Standard Methods for examination of water and waste water", 19th edition, American Public Health Association, 1995

[12] WHO, "Guidelines for the Safe Use of Wastewater, Excreta and Greater", vol. 3. World Health Organisation Press, Geneva, Switzerland, 2006

[13] N.H. Asri and B. Mohammad, "impact of industrial effluents on water quality at the Tiram River", Kuantan, Malaysia, 2015

[14] W.W.Eckenfelder, "Industrial water pollution control", Second edition, McGraw-Hill Book Company, Singapore.1989, ISBN 0-07-100206-5

[15] A. Mdamo, "Accumulation of Nutrients and Heavy Metals in plants at Kagondo natural Wetland" 2001 (Draft Paper). Unpublished.

[16] J.O. Nriagu, "A global assessment of natural sources of atmospheric trace metals". *Nature: International Journal of science*, 1989, 47-49.

[17] I. Simeonov, M. Kolhubovski and B. Simeonov, "Environmental heavy metal pollution and effects on child mental development." Dordrecht, Netherlands: Springer, 2010, Pp 114-115.

[18] S.E.Fendorf, and G.C Li, "Kinetics of chromate reduction by ferrous iron". *Environ Sci Technol*. 1996,;30:1614-1617.

[19] H. Wallace, "Principles and Methods of Toxicology" 2000.

[20] B. Sakar, "Heavy metals in the environment". New York: Taylor and Francis Publishers, 2005