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Article

Qualities of Effluents from Three Cocoa Processing Factories in Ondo State, Southwest Nigeria

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Abstract: Industrial pollution has been and will continue to be a major factor causing the degradation of the environment around us, affecting the land we live on, the water we use and the air we breathe. Effluents from three cocoa processing factories (A, B and C) in Ondo State, Nigeria were analyzed for physicochemical properties, heavy metals and microbial load. The temperature ranged between 28.80^{0}C and 29.40^{0}C. The pH values of the effluents ranged between 6.00 and 6.60. Conductivity of the effluents ranged between 480 and 660µs/cm. The total dissolved solids (TDS) values in the waste water ranged from 198mg/L for factory B, 220mg/L for factory A and 320mg/L for factory C while the total suspended solids (TSS) values ranged from 18.60 to 30.20mg/L. Turbidity of the effluents ranged between 12.2 and 15.50 NTU with C having the highest value. Total hardness of the effluents ranged between 142.00 and 185.00 mg/L$CaCO_3$. Dissolved oxygen levels in the effluents ranged 2.50mg/L and 3.50mg/L. The biological oxygen demand (BOD_5) of the effluents were 26.20mg/L, 20.50mg/L and 18.80mg/L for factories A, B and C, these values fall within Federal Ministry of Environment (FME) effluent limit of 50 mg/L for discharges into inland surface water. Oil and grease was not detected in the effluents. Chemical Oxygen Demand (COD) of the effluents ranged between 58.40 and 75.60 mg/L. Phosphate level in the effluents ranged between 3.60 and 5.00mg/L while nitrate ranged from 14.40- 20.20 mg/L. The mean concentration values of heavy metals ranged for Cu (0.15-0.25)mg/L, Zn (0.02-

0.10)mg/L, Mn (0.05-0.10)mg/L and Fe (0.66-1.20) mg/L. Pb and Cd were not detected. The total bacteria load was too numerous to count (TNTC) cfu/mL while the total Coliform count was 05 mpn/100mL for A, 03 mpn/100mL for B and 08 mpn/100mL for C respectively for the factories. Results were within the federal ministry of environment (FME) limits for effluent.

Keywords: Heavy metals, Microbial load, Effluents, Cocoa Processing Factories.

1. Introduction

Industrialization is vital to a nation's socioeconomic development as well as its political stature in the international committee of nations. It provides ready employment opportunities for good percentage of the populace. Industries vary according to process technology, sizes, nature of products, characteristics and complexity of wastes discharged (Amuda, 2006).

Ideally, citing of industries should strike a balance between socioeconomic and environmental considerations. In developing countries such as Nigeria, the location of industries is determined by various criteria, some of which are environmentally unacceptable, thereby, posing serious threat to public health. Significant in this respect is the establishment of industrial estates alongside residential areas in most state capitals and urban cities in Nigeria.

Rapid industrial development and the world global growth have led to the recognition and increasing understanding of interrelationship between pollution, public health and environment. While most 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 (WHO, 1982).

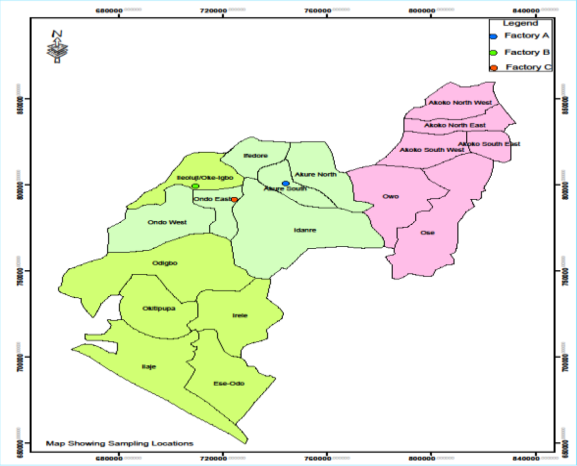
Although industrialization is inevitable, various devastating ecological and human disasters which have continuously occurred over the last four decades, implicate industries as major contributors to environmental degradation and pollution problems of various magnitude (Abdel-Shafy and Abdel-Basir, 1991; Asia and Ademoroti, 2001; Amoo *et al.*, 2004). Wastewater contains offensive and potentially dangerous substances which cause pollution and contamination of the environment and receiving water bodies (Shaw and Schudram, 2000).

It has been reported that industrial effluent has hazard effect on water quality, habitat quality and complex effects on flowing waters (Ethan *et al.*, 2003). Industrial wastes and emission contain toxic and hazardous substances, most of which are detrimental to human health (Rajaram and Ashutosh, 2008a; Rajaram and Ashutosh, 2008b). Other pollutants include heavy metals such as lead, cadmium and mercury, and toxic organic chemicals such as pesticides, PCBs, dioxins, polyaromatic hydrocarbons

(PAHs), petrochemical and phenolic compound (Rajaram and Ashutosh, 2008b) [9]. The focus of this study is to determine the effluents qualities from three cocoa processing factories in Ondo State, Nigeria to know if it complies with regulatory standards of FME.

2. Materials and Methods

Three Cocoa Processing factories were used for this research. They are (A), (B) and (C); all in Ondo State, Nigeria.



S/N	SAMPLE	FACTORY	GPS READIND
1.	Effluent	A	N07^{0}17.002^1 E005^{0}10.159^1
2.	Effluent	B	N07^{0}08.025^1 E004^{0}52.861^1
3.	Effluent	C	N07^{0}11.001^1 E004^{0}52.035^1

GLOBAL POSITIONING SYSTEM (GPS) OF SAMPLING POINTS

Figure 1: Map of Ondo State showing the sampling points

2.1. Effluent Sampling, Storage and Preservation

Effluent samples were collected at the discharged points of three different Cocoa processing factories. Samples for physiochemical analysis were put into 1 liter plastic container, samples for microbiological analysis were taken with sterile sampling bottles while those for heavy metals were taken with 250mL plastic containers and acidified with 0.10M HNO_3. Samples collected were stored at 4 ±2 °C in ice chest on the field before transportation to the laboratory for further storage at 4 ±2 °C.

2.2. In-situ Analysis

Effluent temperature, pH, electrical conductivity and total dissolved solids (TDS) were measured *in situ* using a portable Hanna Combo (combined) meter. Dissolved oxygen (DO) was measured *in situ* using Hanna DO digital meter (WHO, 1982; Leung, 2004).

2.3. Chemical Analysis

2.3.1. Determination of pH

The pH of the collected samples were determined in the laboratory to cross check the field results using pH meter (Jenway 3505 model) after calibration with standard buffer solutions of pH 4 and pH 7 (Hewitt, 2001).

2.3.2. Total solids

2mL of the sample was weighed in a previously weighed Petri-dish. The Petri-dish plus sample was then transferred into the oven set at 105°C to dry to a constant weight for 24 hours overnight, and this was later transferred to the dessicator, cooled, weighed and calculated as described by Hewitt, 2001.

2.3.3. Measurement of turbidity

Hanna portable turbidity meter (HI 98703) was used to determine the turbidity of the effluent samples. The instrument was calibrated with manufacturer’s supplied primary standards before use. The entire visible spectrum (white light) was used; and the complementary colour of the one absorbed was observed as transmitted light (US Clean Water, 1992).

2.3.4. Chloride content

50mL of the sample was transferred using a pipette into a 250mL conical flask and 1mL of K_2CrO_4 was added to it as a reagent; titrated with 0.1M of $AgNO_3$ in the burette with the addition of 1mL of K_2CrO_4, the solution turned brick red. Chloride content was calculated as described by Fergusson, 2000.

2.3.5. Biochemical oxygen demand

Effluent sample was incubated in the dark at 20^{o}C for 5-days using BOD bottles. The difference in oxygen levels between the first and the last is the amount of BOD_5 (APHA, 1992).

2.2.7. Chemical oxygen demand

A predetermined amount of the reference substance dispersed in water was oxidized by potassium dichromate in a strong sulphuric acid medium with silver sulphate as a catalyst, under reflux for two hours. The residual dichromate was determined by titration with standardized ferrous ammonium sulphate. In case of chlorine-containing substances, mercuric sulphate was added to reduce chloride interference (Volesky, 2005).

2.2.8. Sulphate determination

One hundred mililitres (100mL) of the effluent sample was placed in a 250mL erlymenyer flask; 5mL of conditioning reagent was added; while stirring on a magnetic stirrer, a spoonful of $BaCl_2$ crystals was added. Stirring was continued for 1 minute and part of the solution was poured into an absorption cell and the absorbance read at 425nm. Solution of sulphates (2-10mg/L) were prepared from sodium sulphate stock solution and treated as above. Sulphate concentrations were determined by extrapolation from the calibration curve prepared from the standards and calculated as: $SO4^{2-}$ mg/L = mg/L SO_4 read from curve x 1000/ mL of sample (Volesky, 2005).

2.2.9. Phosphate determination

Twenty five mililitres (25mL) of phosphate standard solution and each of the samples were pipetted separately into 50mL volumetric flasks, 10mL of Vanado-molybdate reagent was added and made up to mark with distilled water, full colour was allowed to develop for about 10minutes and absorbance was read at 470nm against a reagent blank. Readings of unknown were read from the standard curve generated and results were calculated (Volesky, 2005).

2.2.10. Determination of Nitrate

Ten (10) mL of the effluent sample was pipette into a spectrophotometer cell and followed by the addition of 1mL nitraver reagent powder. The content was made up to 25mL with deionised water. This was immediately stoppered and shaken vigorously for about 1minute. Amber colour was allowed to develop for 5minutes and the nitrate concentration was read at 500nm against a reagent blank. Nitrate concentration in mg/L was read directly on the equipment (US Clean Water, 1992).

2.2.11. Oil and Grease Determination

Five hundred mililitres (500mL) of effluent sample was put in a separating funnel and the content was acidified with H_2SO_4 using 5mL of acid per liter of sample. The content was mixed by inversion and 25mL of petroleum ether was added into the separating funnel and shaken vigorously for about 2minutes. This led to the separation of organic and aqueous layer. The aqueous layer was withdrawn into a clean beaker while the organic solvent layer was put in a distilling flask. The procedure was repeated thrice to ensure that all of the oil and grease were removed into the solvent layer. The organic solvent layer was distilled off on a water bath, through a condenser and the solvent recovered till it remained about 10mL. The condenser was disconnected and the remaining solvent was evaporated off from the flask by placing it in a water bath set at 100°C to gradually allow the solvent vapour to escape completely. The flask was cooled in a dessicator and weighed. Oil and Grease in (mg/L) was then calculated as described by US Clean Water, 1992.

2.4. Microbial Analysis

Serial dilutions were carried out on each of the effluent samples and were cultured using the pour plate method. Nutrient Agar (NA) was inoculated with 10^{-4} or more dilution of the sample(s) for bacteria and Potato Dextrose Agar (PDA) was inoculated with 10^{-2} or more dilution of the sample(s) for fungi. The NA plates were incubated at 35°C for 24 hours and PDA plates were incubated at 25°C for 48 - 72 hours. For each sample cultured, observation was made on at least one plate of the series whose bacteria or fungi numbers were sufficiently low which allowed the development of well separated colonies. The colonies were sub-cultured until pure cultures of the isolates were obtained and were identified according to Cowan and Steel (1985). These were then stocked for further biochemical analysis. Mac-Conkey broth was used for the determination of coliform counts (Geely and Demark, 1992).

2.5. Metal Analysis

Heavy metals such as Cd, Pb, Zn, Mn, Cr, Cu and Fe were analyzed using Atomic Absorption Spectrophotometer (AAS) Bulk Scientific 210 VGP model. Calcium and Magnesium were determined using EDTA titrimetric method (Volesky, 2005).

3. Results and Discussion

The mean result of the physico-chemical characteristics of the effluent from the three factories were presented in (Tables 1). The temperature of the effluents ranged between 28.80^{o}C and 29.40^{o}C. The values fell below FME effluent limit of <40^{o}C. These values were also within 27.00^{o}C±0.00 to 35.35^{o}C±0.71 reported by Siyanbola (2006) for some selected manufacturing industries in Lagos State, Nigeria.

Conductivities of the effluents were between 480 and 660 μs/cm. Although there is no FME limit values for this parameter. However, the ranged of values obtained were within the range reported for some processing industries elsewhere (Siyanbola, 2006; Alao *et al.*, 2010). Conductivity is a measure of dissolved ions in aqueous solution. The TDS values in the waste water were 220mg/L, 198mg/L and 320mg/L for factory A, B and C respectively. The total suspended solids (TSS) values ranged from 18.60 to 30.20mg/L. The total dissolved solids (TDS) and total suspended solids (TSS) were lower than FME limit for effluent; and lower than 848 – 1840 mg/L and 35 – 1200 mg/L obtained for TDS and TSS respectively for textile industries' effluents in Kaduna (Yusuf and Sonibare, 2004).

Turbidity of the effluents ranged between 10.20 and 15.50 NTU with factory C having the highest value. Turbidity was not specified by FME but the values were similar to 13.20 – 15.00 NTU obtained by Ogbonnaya (2008) for effluents from food processing companies in Lagos but lower than 2.65 – 152.00 NTU obtained for industrial effluents in Ibadan (Fayemiwo and Adebisi, 2011).

The mean pH values of the effluents were 6.20, 6.60 6.00 for factories A, B and C respectively. These results showed that the pH of effluent was tending towards neutral from the acidic region. The recorded pH values for these industries were within the range of 6.00-9.00 recommended by the Federal

Ministry of Environment (FME) for effluent discharge (APHA, 1998). Ogbonnaya (2008) obtained pH values of 6.00 – 8.00 for food processing companies' effluent in Jos and Lagos while Fayemiwo and Adebisi (2011) obtained pH values of 6.50 – 10.20 for industrial effluents in Ibadan, Nigeria.

Table 1. Physicochemical Properties of Effluents from three cocoa processing factories in Ondo State, Nigeria

Parameter	**A**	**B**	**C**	**FMEnv Limit**	
				A	**B**
Temperature (°C)	28.8	29.4	29.0	40	40
Colour (Pt/Co Unit/Odour	Objectionable	Objectionable	Objectionable	7	-
Turbidity (NTU)	12.00	10.20	15.50	-	-
pH	6.20	6.60	6.0	6-9	6-9
Conductivity (μ/cm)	660	480	560	-	
Total Dissolved Solids (TDS) (mg/L)	220	198	320	2000	2000
Total Suspended Solids (TSS) (mg/L)	24.80	18.60	30.20	30	-
Total Solids (mg/L)	244.80	116.60	350.20	-	-
Acidity (mg $CaCO_3$/L)	1.20	1.00	1.60	-	-
Total Hardness (mg$CaCO_3$/L)	158	142	185	-	-
Chloride (mg/L)	58.40	68.70	75.60	600	600
Nitrate (NO^-_3) (mg/L)	18.2	14.40	20.20	-	-
Sulphate (SO_4^{2-})(mg/L)	30.4	26.4	38.1	500	10000
Phosphate (PO_4^{2-})(mg/L)	4.40	3.60	5.0	5	10
Cyanide (CN^-) (mg/L)	ND	ND	ND	0.1	-
Dissolved Oxygen (mg/L)	3.0	3.5	2.5	-	-
BOD_5 (mg/L)	26.2	20.50	18.80	50	500
COD (mg/L)	32.4	28.50	34.20	-	-
Oil and Grease (mg/L)	ND	ND	ND	10	30

ND: Not Detected; FMEnv Limit A- Limit for discharge into surface water, FMEnv Limit B-Limit for discharge into land water

The total hardness mean result of the effluents was 158 mg$CaCO_3$/L for factory A, 142 mg$CaCO_3$/L for factory B and 185 mg$CaCO_3$/L for factory C. There is no FME specification for total hardness but the values were higher than 27.50 – 125.00 mg $CaCO_3$/L obtained for industrial effluents in Ibadan (Fayemiwo and Adebisi 2011).

The dissolved oxygen level ranged between 2.50mg/L and 3.50 mg/L, this result was similar to what Siyanbola (2008) reported (1.73 – 7.51 mg/L) of effluents analyzed from some selected industries in Lagos, but lower than 5.22 – 17.41 mg/L reported by Fayemiwo and Adebisi (2011) for some selected industries in Lagos and Ibadan respectively.

The biological oxygen demand (BOD_5) of the effluents were 26.20mg/L, 20.50mg/L and 18.80mg/L for factories A, B and C respectively, these values fall within FME effluent limit of 50 mg/L for discharges into inland surface water. The values were lower than 227 – 645 mg/L obtained by Yusuf and Sonibare 2004 for effluents from textile industries in Kaduna, but lower than 632.8 mg/L reported for effluent from brewery industry reported by Alao *et al.*, (2010) and 59.00 – 180.00 mg/L obtained for industrial effluents in Ibadan by Fayemiwo and Adebisi (2011). Effluent with high BOD levels when discharged into water bodies will cause depletion of dissolved oxygen level in the water as a result of biodegradation of material substances in the effluent by bacteria in the water body and thereby diminishing dissolved oxygen level to an extent that could endanger many aquatic organisms in the water body (Rajaram and Ashutost, 2008b).

Chemical Oxygen Demand (COD) of the effluents ranged between 28.50 and 34.20 mg/L. There is no FME limit for COD, but the values fall within 36.00 – 160.00 mg/L obtained for industrial effluents in Ibadan by Fayemiwo and Adebisi (20111). Oil and grease was not detected in the effluents from the three factories.

The level of phosphate in the effluents were 4.40 mg/L, 3.60 mg/L and 5.00mg/L for factories A,B and C. Nitrate concentration ranged from 14.40- 20.20 mg/L. The phosphate and nitrate values were lower than 0.09 – 3.42 mg/L and 0.8 – 7.97 mg/L obtained by Yusuf and Sonibare (2004) for effluent from textile industries in Kaduna and 15.33 – 30.67 mg/L and 9.10 – 31.80 mg/L obtained for the effluent from Odua textile mill, Ado Ekiti, Nigeria.

The mean concentration values of heavy metals ranged for Cu (0.15-0.25)mg/L (table 2). Copper plays an important role in biological and chemical processes in the environment (Sharma *et al.*, 1988). The concentration of copper was within WHO limit of 1.00mg/L and <1.00mg/L for FME standard. Excess copper intake causes stomach upset, nausea, and diarrhea and can lead to tissue injury and disease (Volesky, 2005). The values of trace metals are in accordance with Akan *et al.*, (2007); Bichi and Anyata (1999). The concentration of Zn ranged between (0.02-0.10) mg/L. Although, zinc is essential for human health but too much Zn can cause health problems, like stomach cramps, skin irritation, vomiting, nausea and anemia. There is no WHO and FME limits for Zn, Ca, Mg and Cr. The concentration of manganese were 0.10 mg/L, 0.05 mg/L and 0.15 mg/L while Fe were 0.80 mg/L , 0.66 mg/L and 1.20 mg/L for effluents from factories A, B and C respectively. Pb and Cd were not detected. The absence of Cadmium and Lead could be due to the absence of the metals from the raw material in use at the time of sample collection. Lead poisoning could cause abdominal pain, loss of appetite, insomnia and constipation. Severe kidney as well as brain damage has been reported on long term exposure Bichi and Anyata (1999).

Chromium is an essential nutrient for humans its shortage may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much chromium can cause problems to health (Moore, 1991). Numerous industrial applications raised chromium to very important economic element. The health hazards associated with exposure to chromium are respiratory problems, a lower ability to fight disease, birth defects, infertility and tumor formation. The toxicity of chromium is dependent on its oxidation state. The metal form is of low toxicity but hexavalent form is toxic. The higher concentration of chromium attributed to application of chromium compounds as a catalyst in many industrial applications. Iron is non-toxic and an essential element in human nutrition (Fasoto *et al*., 2014).

Table 2: Heavy metal concentration of effluent from three cocoa processing factories in Ondo State.

Metal [mg/kg]	A	B	C	WHO Standard	FMEnv Standard
Pb	BDL	BDL	BDL	0.01	<1.0
Cu	0.20	0.15	0.25	1.0	<1.0
Mn	0.10	0.05	0.15	0.5	5.0
Fe	0.80	0.66	1.20	0.3	
Cd	BDL	BDL	BDL	0.003	
Cr	0.02	0.05	0.04		
Zn	0.05	0.02	0.10		
Ca	30.20	26.80	32.00		
Mg	18..40	20.00	22.80		

WHO: World Health Organization, **BDL:** Below Detection Limit, **FMEnv:** Federal Ministry of Environment

The total bacteria count of the effluents from the three factories were too numerous to count (table 3). The total coliform count were 05 mpn/100mL, 03 mpn/100mL and 08 mpn/100mL for factories A, B and C respectively. This is different from the result got from a brewery effluent in Ibadan, South West Nigeria by Olorode *et al.*, (2012) where the bacteria count ranged from 180 x 10^3 cfu/ml to 150 x 10^3 cfu/ml and their total coliforms ranged from 2.0 x 10 mpn/100mL to 7 x 10 mpn/100mL.

Table 3: Microbiological test on Effluent from three cocoa processing factories in Ondo State

Test	A	B	C
Total Bacteria Count [cfu/mL]	TNTC	TNTC	TNTC
Total Coliform [mpn/100mL]	05	03	08

TNTC: Too numerous to count

4. Conclusions

This study on the qualities of effluents from three different cocoa industries revealed conformance in most parameters with the FME national standards for effluent. It is important that factories should have systems in place for the treatment of effluents before discharged to the environment in ensuring the sustainability of aesthetic environment.

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