

## Characterization of Warri Refinery Effluent and its Recipient Medium

Nwaichi, E. O.\*, Essien, E. B. and Ugbeyide, E.

Department of Biochemistry, University of Port Harcourt, Port Harcourt, P. M. B. 5323 Port Harcourt, Rivers State, Nigeria

\*Corresponding Author Email: nodullm@yahoo.com

### ABSTRACT

*This study examines some physico-chemical parameters in Warri refinery effluent and its effect on the receiving Iffie River. The data that were used in this study were generated from direct field measurements and laboratory analysis. Recorded mean pH values of the treated and untreated effluents, and receiving water body were  $7.79 \pm 0.04$ ,  $8.25 \pm 0.02$ ,  $7.84 \pm 0.01$  (upstream),  $7.84 \pm 0.01$  (downstream) and  $8.02 \pm 0.01$  (point of discharge) respectively. Temperature ranged from  $25.75^{\circ}\text{C}$  -  $27.30^{\circ}\text{C}$  in all samples. The turbidity value for the treated effluent was  $3.30 \pm 0.01$  NTU and  $7.50 \pm 0.06$  NTU for the untreated effluent while that of the receiving Iffie River ranged from 14.60 – 16.20 NTU. Electrical conductivity ranged from 137 – 108  $\mu\text{S}/\text{cm}$  for the treated and untreated effluents and mean values of  $52.13 \pm 1.53$ ,  $52.50 \pm 2.50$  and  $73.33 \pm 0.88$  for the upstream, downstream and point of discharge sections respectively indicating natural dilutions. Total hydrocarbon (THC) and total dissolved solids (TDS) varied from maximum values of 10.24 and 170.00 mg/l respectively. It was observed that the untreated effluent had more statistically significant phenol content ( $29.86 \pm 0.07$ ) than those of the treated effluent ( $8.44 \pm 0.02$ ) at  $p = 0.05$  while cyanide concentration was higher than the WHO limit (0.07 mg/l) for waste water. Although significant improvements were evident in some water quality parameters, elevated levels of major refinery contaminants, hydrocarbons and phenol in treated effluent is indicative of ineffectiveness of purification systems.*

**Keywords:** Effluents, Iffie River, Water quality, Phenol, Refinery, Upstream, Downstream.

### INTRODUCTION

Petroleum refinery and petrochemical industries are most desirable for national development and improved quality of life. However, pollution effects<sup>1</sup> of the petroleum waste from these industries are causes for worry. The waste water released from the refineries are characterized by the presence of large quantities of crude oil products, polycyclic and aromatic hydrocarbon, phenols, metal derivatives, surface active substances, sulphides, naphthalene acids and other chemicals<sup>2</sup>. Phenol is readily absorbed through the skin, mucous membranes<sup>3</sup>, and gastrointestinal tract, and is rapidly excreted by the kidneys. Oral administration of undiluted phenol can cause necrosis and hemorrhage of mucous membranes. Systemic poisoning is manifested by headache, dizziness, tinnitus, vertigo, tremors, twitchings, and convulsions<sup>4</sup>. In subacute poisonings, anorexia, nausea, and vomiting may occur. Lethal dosage ranges from 80 mg/kg to 1,300 mg/kg. Based on chronic toxicity data on animals, ambient water criteria proposed by the Environmental Protection Agency in 1979 are 3.4 mg/l, allowing for an approximate 7 mg/day intake. In areas of chlorination, a level of 0.001 mg/l is suggested, based on the objectionable taste and odor produced by chlorinated phenols, which have a taste threshold of 0.005 mg/l<sup>5</sup>. As a result of ineffectiveness of purification systems, waste water may become seriously dangerous, leading to the accumulation of toxic products in the receiving water bodies with potentially serious consequences on the ecosystem<sup>6,7</sup>.

The uncontrolled disposal of waste into water renders water unsafe for economic and recreational uses and pose threat to human life and it is also against the principle of sustainable development. Water borne diseases and water related health problems are mostly due to incompetent management of water resources. Safe water for all can only be assured when access, sustainability and equality can be guaranteed <sup>8,9</sup>. The risks of environmental contamination caused by volatile organic compounds have driven a lot of research designed to eliminate or remedy its deleterious effects. Several of these compounds, such as phenol and BTEX compounds (benzene, toluene, ethyl benzene and the isomers of xylene) are found in effluents from oil refineries, and they are important contaminants due to their high toxicity <sup>10</sup>.

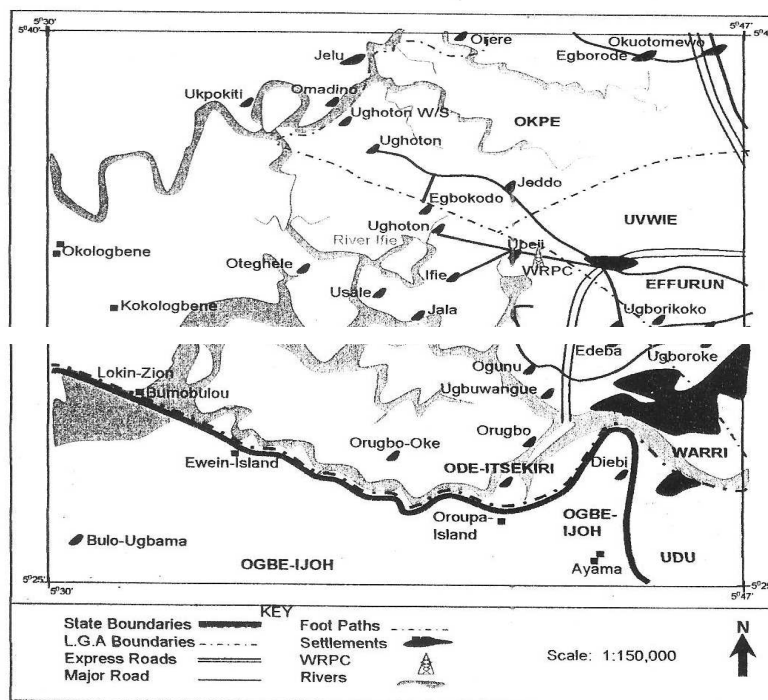
Refinery effluent containing oil when discharged into water body can cause depletion of dissolved oxygen due to transformation of organic component into inorganic compounds, loss of biodiversity through a decrease in amphipod population that is important in food chain and eutrophication. Short term toxicity in fishes includes lymphocytosis, epidermal hyperplasia, and hemorrhagic septicaemia <sup>11</sup>. It has been reported that large amount of oily materials in soil increased the temperature by 1 to 10°C <sup>12</sup>. Oil has been found to change the soil pH. Warri Refinery Petrochemical Company, WRPC is one of the few Refineries in Nigeria. Since, it is a known fact that refinery effluents contains mutagenic, carcinogenic and growth inhibitory substances which adversely affect the ecology of aquatic and terrestrial ecosystems, it therefore becomes imperative to study the physico-chemical parameters of the WRPC effluents and inherent discharge effects.

**METHODOLOGY**

**Study Area**

Warri refining and petrochemical company is located in Ekpan, Delta State and it is a subsidiary of the Nigerian National Petroleum Cooperation (NNPC). The refinery is bounded by three communities Ekpan, Jeddo and Ubeji. Ifie is next to Ubeji (Fig. 1). The study area is located around latitude 5°31'N and 6°11'N and between longitude 5°44'E and 5°47'E. The area is approximately 100 square kilometers and it is bounded by other communities. Human activities around the refinery are primarily fishing, farming, and petty trading.

**FIG 1: MAP OF WARRI SOUTH SHOWING STUDY AREA (Source: Atubi, 2011)**



### Sample Collection

The effluent samples (treated and untreated) were collected in triplicates from Warri Refinery and petrochemical company into clean 1 litre plastic containers. Breakable bottle containers were used for THC samples. Unstable pH and temperature were analysed on site using portable meters. Water samples were also collected from Iffie River in the neighboring community where the refinery discharges its effluents. Water quality parameters like pH, Temperature, Turbidity, TDS, DO, BOD, COD, Electrical conductivity, TSS, Salinity, Phenol, CN etc. were investigated. Three sampling points (Point of discharge (PD), upstream (US) and downstream (DS) locations) were used and the sampling points are approximately 1km away from each other. The samples were stored in an ice box of 4°C and taken to the laboratory within twenty-four hours for analysis. Level of pH was measured with Hanna pH meter, conductivity was measured with the Suntex conductivity meter, Total Dissolved Solids (TDS) was measured with the Hatch TDS meter, model CO20, Total Suspended Solids (TSS) was determined using weight loss technique and turbidity was measured with hatch Spectrophotometer, model DR2010. Others were by APHA standard testing methods.

### Statistical Data

Data was analysed using descriptive statistics. Analysis of variance (ANOVA) was used to test for significant differences at  $P \leq 0.05$ . The treatment means were separated using Duncan's multiple range test (DMRT)

## RESULTS AND DISCUSSION

The results of the physico-chemical analysis performed on the effluents from WRPC and its recipient Iffie river are as shown in Tables 1 and 2.

**Table 1: Physico-chemical composition of refinery effluent**

S/N	Parameter(s)	Treated effluent	Untreated effluent	WHO STD
1.	pH	7.79± 0.04 <sup>(a)</sup>	8.25± 0.02 <sup>(b)</sup>	6.5 – 9.6
2.	Temperature (°C)	25.75± 0.15 <sup>(c)</sup>	27.30± 0.70 <sup>(b)</sup>	30
3.	Conductivity (µs/cm)	108± 2.0 <sup>(b)</sup>	137± 2.0 <sup>(b)</sup>	500
4.	Salinity (mg/l)	27.58± 0.52 <sup>(a)</sup>	11.65± 0.15 <sup>(b)</sup>	NA
5.	Turbidity (NTU)	3.30±0.01 <sup>(c)</sup>	7.50±0.06 <sup>(b)</sup>	5.82
6.	THC (mg/l)	3.69± 0.25 <sup>(b)</sup>	10.24± 0.25 <sup>(c)</sup>	NA
7.	TSS (mg/l)	16.00± 0.47 <sup>(b)</sup>	40.00± 0.47 <sup>(c)</sup>	30
8.	TDS (mg/l)	66.00± 1.0 <sup>(a)</sup>	170.00± 0.475 <sup>(c)</sup>	500
9.	COD (mg/l)	1.89± 0.01 <sup>(c)</sup>	1.89± 0.01 <sup>(c)</sup>	40
10.	BOD (mg/l)	0.60±0.05 <sup>(a)</sup>	1.50±0.05 <sup>(a)</sup>	1.0
11.	DO (mg/l)	4.19± 0.18 <sup>(c)</sup>	3.11± 0.18 <sup>(c)</sup>	4-5
13.	Phenol(mg/l)	8.44±0.02 <sup>(d)</sup>	29.86±0.07 <sup>(b)</sup>	0.2
13.	CN(mg/l)	0.008±0.001 <sup>(b) (a)</sup>	0.10±0.001 <sup>(b) (a)</sup>	0.07

Data are presented as MEAN ± SEM, n=3.

Means with the same superscript in the same row are not statistically significant at ( $P \leq 0.05$ ).

WHO standard is included for comparison.

The physicochemical qualities of the major effluents generated in the Warri refinery were investigated, and the level of contaminants estimated. The concentration of the most significant pollutants in the various refinery effluents are shown in Table 1. The results of our study revealed that the effluents have a pH range on average between 7.79 and 8.25. The alkaline nature of the effluent may be due to the presence of soluble organic and inorganic alkalis. These pH values are within the World Health

Organization standards (WHO) set limit, 6.5 - 9.6 of wastewater which must be discharged into the sea or environment (WHO, 2006). Electrical conductivity of water samples is used as an indicator of how salt free, ion free or impurity free the sample is. It is very important for the control of wastewater pollution level. The purer the water, the lower the conductivity. The higher conductivity value which was recorded for the untreated effluent sample (137  $\mu\text{S}/\text{cm}$ ), may be due to the discharge of chemicals used in refining of petroleum products. The conductivity value of the treated effluent gave 108  $\mu\text{S}/\text{cm}$ .

**Table 2: Characteristics of Iffie river**

S/N	Parameter(s)	US	PD	DS	WHO STD
1.	pH	8.02 $\pm$ 0.01 <sup>(b)</sup>	7.84 $\pm$ 0.01 <sup>(c)</sup>	7.84 $\pm$ 0.01 <sup>(c)</sup>	6.5 – 9.6
2.	Temperature ( $^{\circ}\text{C}$ )	26.47 $\pm$ 0.45 <sup>(a)</sup>	26.50 $\pm$ 0.21 <sup>(a)</sup>	26.50 $\pm$ 0.30 <sup>(a)</sup>	30
3.	Conductivity ( $\mu\text{S}/\text{cm}$ )	73.33 $\pm$ 0.88 <sup>(e)</sup>	52.13 $\pm$ 1.53 <sup>(f)</sup>	52.50 $\pm$ 2.50 <sup>(f)</sup>	500
4.	Salinity (mg/l)	5.40 $\pm$ 0.15 <sup>(e)</sup>	5.37 $\pm$ 0.22 <sup>(e)</sup>	3.56 $\pm$ 0.06 <sup>(e)</sup>	NA
5.	Turbidity (NTU)	15.46 $\pm$ 0.12 <sup>(b)</sup>	16.20 $\pm$ 0.25 <sup>(b)</sup>	14.6 $\pm$ 0.10 <sup>(b)</sup>	5.82
6.	THC (mg/l)	<0.001 <sup>(b)</sup>	<0.001 <sup>(b)</sup>	<0.001 <sup>(b)</sup>	NA
7.	TSS (mg/l)	14.00 $\pm$ 0.10 <sup>(b)</sup>	15.00 $\pm$ 0.13 <sup>(b)</sup>	13.00 $\pm$ 0.12 <sup>(b)</sup>	30
8.	TDS (mg/l)	34.64 $\pm$ 0.18 <sup>(e)</sup>	31.70 $\pm$ 0.20 <sup>(e)</sup>	27.60 $\pm$ 0.30 <sup>(e)</sup>	500
9.	COD (mg/l)	0.31 $\pm$ 0.02 <sup>(f)</sup>	0.38 $\pm$ 0.01 <sup>(e)</sup>	0.33 $\pm$ 0.15 <sup>(f)</sup>	40
10.	BOD (mg/l)	0.20 $\pm$ 0.01 <sup>(c)</sup>	0.25 $\pm$ 0.01 <sup>(c)</sup>	0.23 $\pm$ 0.02 <sup>(c)</sup>	10
11.	DO (mg/l)	3.18 $\pm$ 0.01 <sup>(a)</sup>	3.17 $\pm$ 0.01 <sup>(b)</sup>	2.92 $\pm$ 0.00 <sup>(d)</sup>	10
12.	PHENOL(mg/l)	<0.001 <sup>(a)</sup>	<0.001 <sup>(a)</sup>	<0.001 <sup>(a)</sup>	0.2
13.	CN(mg/l)	<0.001 <sup>(a)</sup>	<0.001 <sup>(a)</sup>	<0.001 <sup>(a)</sup>	0.07

According to the World health organization standard, the temperature of both effluent and river samples were below the permissible limit of 30 $^{\circ}\text{C}$ . When an organic matter undergoes decomposition, some part is readily used within 48 hours by microorganisms known as Biochemical Oxygen Demand (BOD) and the other complex part called the Chemical Oxygen Demand (COD) gets slowly decomposed. Since both these parameters give clue of the total organic load, therefore they are quite essential for the assessment of effluent quality. The COD and BOD concentrations of treated effluent samples were within WHO given limits. There was significant difference between the turbidity values of the treated effluent (3.3 NTU) and the untreated effluent (7.50 NTU) at  $P \leq 0.05$ . Dissolve oxygen, DO which is the quantity of oxygen used in aerobic oxidation of organic matter, was 4.19 mg/l for the treated effluent and 3.11 mg/l for the untreated effluent sample. The low DO concentration observed in the receiving water could be due to the presence of other decaying substances such as dead algae and human wastes from the residents of the community.

The values of the total dissolved solids of the samples was satisfactory as they fell within the WHO specified limit (500 mg/l). however, significant decreases were observed with treatment and natural dilution. The mean value of total hydrocarbon (THC) as shown was high in the untreated effluent (10.24 mg/l) and reduced in the treated effluent sample (3.69 mg/l). High TSS value for the untreated effluent, 40.00 mg/l, which was higher than the WHO recommended value for waste water (30 mg/l) was reduced to a value of 16 mg/l with treatment.

Phenol is one of the major pollutants found in refinery effluents (World bank, 1998). It was found in high concentrations in both the treated and the untreated effluents. The observed values for phenol of 8.44 mg/l

in the treated effluent and 29.86 mg/l in the untreated effluent respectively were much higher than the 0.2 mg/l WHO recommended standard. Natural dilution may be responsible for the insignificant amount of phenol present in the river samples (<0.001 mg/l) (table 2). The cyanide concentration of the treated effluent gave 0.008 mg/l, 0.10 mg/l for the untreated effluent and <0.001 mg/l (table 2) for the river sample.

Turbidity values did not conform with the maximum acceptable limit (5.82 NTU) for wastewater (WHO, 2006). The turbidity values at the point of discharge (16.20 NTU) was higher than both the downstream (14.6 NTU) and upstream sections (15.46 NTU). This can pose serious injurious effect on ecosystem (Nwaichi and Wegwu, 2010) and may be attributable to other human activities and decaying of plant and animal materials.

The concentrations of the pH showed that the effluents have no adverse impact on the receiving environment which had a pH range of 7.84 – 8.02. These results compare with the findings of Ademoroti (1983), who found similar results on the influences of effluents in Ibadan. Electrical conductivity value at the point of discharge was 52.13  $\mu\text{S}/\text{cm}$  while 73.33  $\mu\text{S}/\text{cm}$  and 52.50  $\mu\text{S}/\text{cm}$  were recorded for upstream and downstream samples respectively. The salinity values measured (5.37 mg/l for PD, 5.40 mg/l for US and 3.56 mg/l for DS) were low when compared to those of the effluents and could be dilution influences.

### CONCLUSION

The results obtained from this study showed high Phenol and Hydrocarbon load from WRPC effluents although most of the physicochemical parameters studied were within the desirable limit for effluent disposal on surface waters recommended by WHO. In view of this, more concerted effort at informed - effluent treatment and monitoring is required before discharges into the surrounding aquatic environment. Remedial measures also need to be put together as well as community engagements for synergetic approach.

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