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Efficiency of Pollutants removal in Effluent water treatment units of Port Harcourt Refinery, Rivers State, Nigeria

*Daniel, E.A.; **Fekarurhobo, G.K.; ***Ede, P.N.; ****Igwe, F.U.

***Department of Chemistry, Faculty of Science, Rivers State University, Port Harcourt, Nigeria.*
****Department of Biochemistry, Faculty of Science, Rivers State University, Port Harcourt, Nigeria.*
*****Institute of Geosciences and Environmental Management, Rivers State University, Port Harcourt, Nigeria.*

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ABSTRACT

The efficiencies of the sub-units of the wastewater treatment unit of the Port Harcourt Refining Company Limited were calculated to determine the efficiency of pollutants removal in effluent water treatment units of the refinery. The physicochemical parameters such as pH, oil and grease, phenols, phosphates, sulphides and metal ions (Cr, Pb, Cu, Zn and Fe) were identified as pollutants and measured by standard methods. These parameters were analyzed using the gravimetric and volumetric methods and the heavy metals were determined by atomic absorption spectrophotometry (AAS-6300 model). The bio-treatment sub-unit showed efficiencies of 75.94 and 91.33% in the dry and rainy season by reducing the phenolic compounds from 43.51ppm to 10.47ppm and from 22.73ppm to 1.97ppm respectively. The Dissolved Air Floatation (DAF) sub-unit gave efficiencies of 64.88 and 61.21% in the coagulation and skimming processes to reduce the oil and grease in the dry and rainy season respectively. These results showed that the wastewater treatment unit is efficient in removing the pollutants from the effluent water generated from the refining processes.

Keywords: Port Harcourt, Refinery, Biological Treatment, Dissolved Air Floatation (DAF), Raw Water Biodisk (RWBD), Treated Water Biodisk (TWBD), Raw Water DAF (RWD), Treated Water DAF (TWD), Open Channel Water(OPCH) and Observation Pond (OBSP)

I. INTRODUCTION

Effluent has been described as the liquid waste of sewage and industrial processing liquid which flows away from a containing space or a main waterway (Daniel, 2004). A petroleum refinery is made up of several inter-related processes which separate, alter, arrange and rearrange the molecular configuration of hydrocarbons into various compounds and complexes to meet the economic demands (Speight, 2005). The products from the refineries range from the intermediate products: straight run gasoline (SRG), straight run naphtha (SRN), reformate, fluid catalytic cracking gasoline (FCCG) alkylate, climate, light diesel oil (LDO) heavy diesel oil (HDO), atmospheric residue etc to finished products such as liquefied petroleum gas (cooking gas), premium motor spirit (PMS), kerosene (HHK/DPK/ATK), automotive gas oil (AGO), fuel oil (HPFO and LPFO).

During refining, several substances are used to aid and facilitate the different processes. Water is used for cooling, heat exchange, cleaning and washing. This water at the completion of its purpose has to be discharged to the environment. This effluent water contains numerous organic and inorganic impurities, which are harmful to health and detrimental to the environment especially the recipient aquatic environment. The Department of Petroleum Resources (DPR) is saddled with the responsibility of monitoring the discharges from the refinery to ensure compliance. It is the presence of these contaminants in the effluent water that changes the nomenclature to waste water.

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The DPR discharge limitations for treated petroleum refinery waste water are shown in Table 2.

Water may be the most reusable and recyclable commodity on earth. The supply of potable water may be limited, hence, the need to recycle and reuse it effectively (Hardam, 1976).

Besides water, there are innumerable chemicals that are used for diverse purposes in the refinery and the petrochemical industry. These chemicals are used as solvents, additives, inhibitors, catalysts, softeners, etc for the ultimate processing of hydrocarbons which produce several other grades of hydrocarbons for machines and industries. The reactions among these chemicals and other natural elements such as oxygen, hydrogen, sulphur and even carbon, synthesize obnoxious compounds which send negative signals to the ecosystem. The chemical wastewater which is a major waste treated in the biological section of the Wastewater Treatment Unit (WWT) to produce bio-sludge as effluent, carries the aforementioned chemicals.

Crude oil itself and its vapours are not environment friendly, yet it is the major source of energy to the world and its various applications have considerably downsized the world's unemployment burden. The refinery employs labour but also pollutes the environment. How to manage these two sharp ends simultaneously is a big task for scientists to grapple with.

Sources and Type of Waste Water

Sanitary Waste Water

This refers to sewage from washrooms, canteens, lavatories, etc. In the refinery, about 15% of Biological Oxygen Demand (BOD) materials (H_2S, mercaptans, phenol, etc) are said to come from sanitary waste water (Daniel, 2004). It is best disposed of by draining it into a public sewer system in Nigeria.

Oily Sewer Water

During leakages from pumps and exchangers and spill, the oil flows into the sump pit before it is routed to the oily sewer. This oily sewer contains water too and this mixture forms slurry which is eventually sent to the oil separator in the waste water treatment unit, where the oil is skimmed out and routed to the sump pit.

Chemical Waste Water

Most mineral acids in refinery and petrochemical wastewater are strong acids such as sulphuric acid, nitric acid, phosphoric acid while the weaker ones are carboxylic acid and carbonic acid etc. The acidity of waste water is its capacity to donate protons and this is vital in waste water treatment because neutral or near-neutral water is required before biological treatment can be effective and many regulatory authorities like Department of Petroleum Resources (DPR) and FEPA have criteria which establish strict pH limits for final discharges (FEPA, 1992). Several caustic compounds containing sodium, calcium, potassium and nitrogen in the form of ammonia also contribute alkalinity in refinery waste water. The presence of inorganic dissolved anions in solution such as chlorides, sulfates, nitrates and phosphates is also confirmed in refinery waste water, especially during the quality control of cooling tower and boiler blowdown waters. Regulatory agencies also check the salt concentrations in effluents, especially when it is discharged to fresh receiving waters (Hardam, 1976).

There are also some surface-active substances, which are found in refinery effluent water (Daniel, 2004). Some are water soluble while others are oil-soluble. The water-soluble or hydrophilic group is made up of one of the following groups: anionic group consisting of sulphonates, sulphates, carboxylic acid groups. The cationic groups consist of amine salts and ammonium compounds while the non-ionic groups are alcohols and glycols. These organic compounds don't ionize but are water-soluble.

Process Waste Water

This refers to the sulphide-laden water or "sour water" from process areas. Many petroleum products are steam-stripped or have aqueous washes during refining. This process water therefore contains residual of hydrocarbons, sulphides, ammonia, phenols and caustics. These impurities, define this water as wastewater.

Ballast Water

This is water used in the ship for tank cleaning and to balance the ship while sailing. This water often contains oil and impurities associated with oil. It should normally be routed from the jetty to the refinery for the oil to be separated from the water. But some defaulters discharge their ballast directly to the oceans.

Materials and Methods

Description of Study Area

Port Harcourt Refining Company Limited is located at the latitude of 4.7645°N, and longitude of 7.0997°E in Alesa-Eleme in Eleme Local Government Area of Rivers State. The refinery is situated about 25 kilometers East of Port Harcourt and 10 kilometers away from Eleme Junction in Port Harcourt Township (Figure 1).

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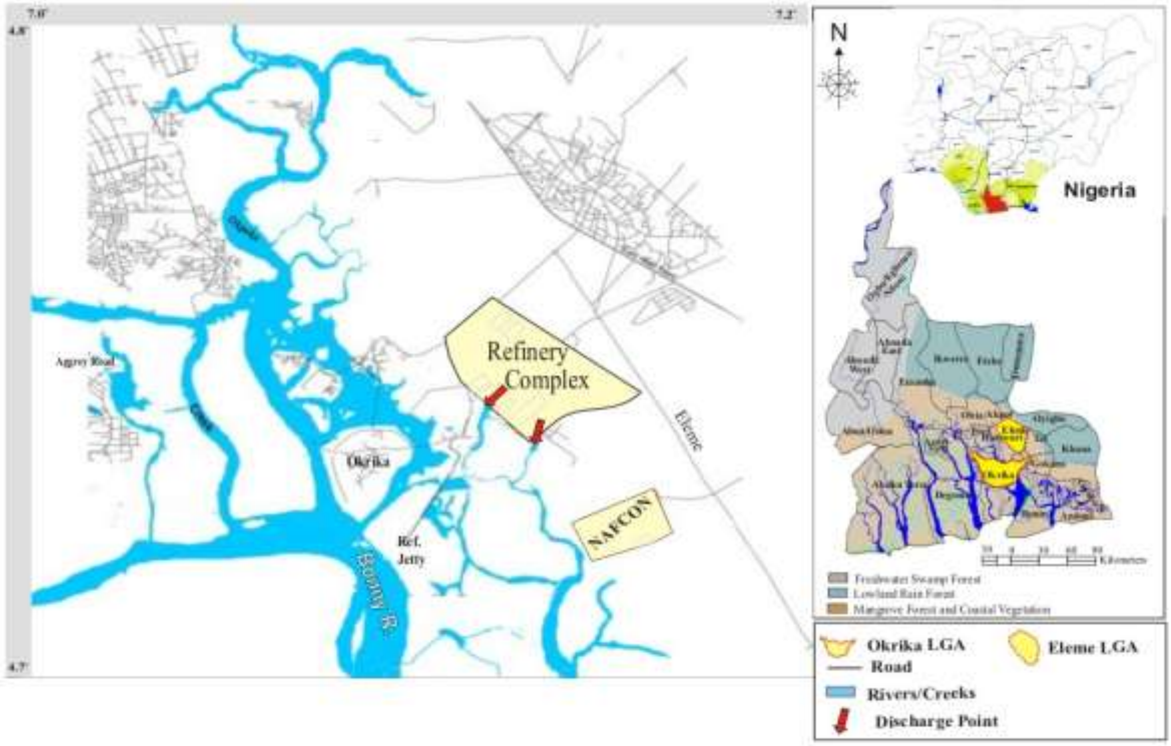

Figure 1: Refinery Complex within Port Harcourt, Rivers State, Nigeria

Sampling and Data Acquisition

This study was carried out in the Wastewater Treatment Unit (WWTU) of the Port Harcourt Refinery which has two major sub-units; the biological treatment sub-unit and the dissolved air floatation sub-unit. The focus was on the pollutants removal efficiency in the effluent water treatment units of the refinery. Transparent polyethylene containers were used to collect the water samples; each having a capacity of 2 litres and with broad openings. They were thoroughly washed with detergent solution, thoroughly rinsed with water and de-ionized water and air-dried before use. The containers were rinsed with the samples 3 times before sampling. Sufficient air space was left to allow for expansion of water at elevated temperatures. Care was taken to ensure the samples were directed gently to the mouth of the containers to prevent spill to the body.

Samples for metal analysis were collected in 2L polyethylene containers and acidified with concentrated nitric acid (4.5mls/litre of sample) to arrest further chemical and physical reactions such as oxidation, reduction, precipitation, adsorption, ion exchange and other surface reactions.

For dissolved oxygen samples, fixation method was used to avoid loss of oxygen from the samples. Care was taken to ensure that no air space is left in the bottles and 2ml of alkaline iodide-acid solution was added at the bottom, using a pipette. The bottles were rinsed and sealed with cello tape to prevent air from entering the bottles. The bottles were carefully transported to the laboratory for analyses.

The samples, Raw Water Biodisk (RWBD), Treated Water Biodisk (TWBD), Raw Water DAF (RWD), Treated Water DAF(TWD), Wastewater Treatment (WWT), Open Channel (OPCH) and Observation Pond (OBSP) were collected from the wastewater treatment unit of Port Harcourt Refining Company, Alesa-Eleme in February, 2018 and July, 2018.

The pH (ASTM D1293-84) was determined using the Meter-Potentiometric Titrator, (PSU-118M 210 KYOTO Electronics) and plastic beakers. The meter was standardized by the buffer solutions of pH 4.01 and 9.18. The electrodes were washed with distilled water, rinsed with ethanol and distilled water again. The water sample was poured into a 200ml beaker to the 100ml mark and the electrodes inserted in it. The beaker was swirled and the pH meter reading allowed to stabilize and recorded.

The oil and grease was analyzed using the method, ASTM D4281. The beakers were dried in the oven for two hours at 120^{o}C and cooled in the desiccators (over drying agent). These beakers were labeled according to the waste samples to be

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analysed and weight of empty beaker recorded as weight A.

200ml of water sample was poured into the separator funnel marked for the sample. 5mls of conc. HCl and 40ml of $CC1_4$ was added. The separator funnel was covered and shaken 5 times with intermittent inversion and opening of tap to release the trapped gas.

The solution in the separator funnel was allowed to stand and separate into layers. The bottom $CC1_4$ layer containing the oil/grease was run into the labeled dry beaker and allowed to evaporate to dryness on a thermostat hot plate at 105^0C in a fume cupboard. The beaker was allowed to cool to room temperature and weight recorded as weight B.

The amount of oil/grease in the water sample was calculated as follows:

$$oil / grease\,(ppm) = \frac{WtB - WtA \, x \, 10^6}{Volume \; of \;\; sample \, (200ml)}$$

Where:

Wt A = Weight of Empty Beaker

Wt B = Weight of Beaker and Residual Oil/Grease

Precaution: The concentrated HCI and CCl4 were handled carefully to avoid its spill on the skin and inhalation, which can lead to severe health problems, especially lung infection. The phenolic compounds were determined spectrophotometrically by ASTM D1783 method using UV-3600 Plus, Schimadzu. The glassware were washed with detergent solution and rinsed with water, chromic acid and distilled water. 100mL of the water sample (e.g. raw water biodisk, RWBD) was measured into the beaker. Three drops of methyl red indicator were added to the sample to check acidity. Three drops of phosphoric acid were also added. 12mL of distilled water was also added to avoid distilling to dryness and the solution distilled for 1 hour during which100mL of distillate was collected. To the 100mL distillate was added 3mL of ammonia buffer solution, 2mL of 4-aminoantipyrine and 2ml of ferric cyanide and allowed to stand for 10 minutes. The blank was prepared by taking 100ml of distilled water and adding all the reagents that were added to the distillate. UV-spectrophotometry was used to scan the solution at 510 nanometer wavelength. The blank sample was used as reference to zero the instrument before scanning the sample. The concentration of phenols in the sample was displayed on the accessory computer screen (CARRY IE UV-Visible spectrophotometer, VARIAN EL97063590) with the absorbance value. The concentration was recorded in ppm. The Sulphide in the Wastewater was analyzed by Iodometric Method. A 100mL measuring cylinder and 250mL conical flask were washed with detergent solution and rinsed thoroughly with tap water and distilled water. 100mls of the sample was measured into a 250ml conical flask. 20mls of 0.05N Iodine solution and 5ml of 6M HCl were added. 0.5ml of starch solution was added and the solution was titrated against 0.025N Sodium Thiosulphate solution ($Na_2S_2O_3$).

Calculation:

Sulphide Concentration, mg/L= (volume of I_2 × N of I_2)-(TV × N of $Na_2S_2O_3$) × Eq. wt of Sulphide × 10,000/volume of sample

Where N= normality, TV= Titre Value or burette reading, Eq. wt= Equivalent weight (17), I_2=Iodine

The metals were measured using atomic absorption/flame emission spectrophotometer, (AAS 670, Shimadzu Corporation), Japan. Standard solutions of lead (Pb), nickel (Ni), copper (Cu), Zn and iron (Fe), each at gradient concentrations of 0.1ppm, 0.2ppm, 0.3ppm, 0.4ppm and 0.5ppm were used. The air-acetylene and nitrous oxide were used as fuels to provide the flame and hollow cathode lamps as light sources.

The instrument was zeroed using distilled water. The instrument was calibrated by measuring the absorbance values of the various concentrations of each of the metals in the respective standard solutions, recording each of the readings by pressing the STANDARD button. The absorbance values of the water samples were measured by pressing the MEASURE button. The absorption values and concentration of the metals of the samples were recorded.

Data Analysis

The statistical means and standard deviations of the results were calculated and used to analyze the data. Data were presented in Tables for clarity purposes

II. RESULTS AND DISCUSSION

Efficiencies of Pollutants Removal in Effluent Water Treatments

The efficiencies of pollutants removal in effluent water treatment units of the Port Harcourt Refinery are shown in Tables 1, 2, 3, 4, 5, 6, 7, 8 and 9. The information on Table X (after Table 9) for DPR Standards for Discharge Limitations for

Treated Petroleum Refinery Waste water serves as guidelines for the study.

Table 1 revealed that the pH levels of the influents of the biological sub-unit, Dissolved Air Floatation and Observation Pond measured in weeks 1-4 of February, 2018 ranged from 7.04 in RWBD and RWD in week 1 to 8.60 at OBSP in week 4. The mean values of 7.92, 7.42, 7.55, 7.42 and 7.90 were observed for the units RWBD, TWBD, RWD, TWD and OBSP respectively (Table 1.1). Corresponding pH values for July ranged between 6.90 for TWBD in week 4 to 9.29 for TWD in week 1. The means of pH values for the unit were 8.18, 7.76, 8.26, 8.21 and 7.73 for RWBD, TWBD, RWD, TWD and OBSP respectively. The pH mean values of 7.42-8.26 for the two seasons are within the range (6.5-8.5) for optimum microbiological treatment effectiveness (https://www.ebsbiowizard.com , 2018).

The pH mean values of 7.73 and 7.90 observed for OBSP in July and February respectively are within the DPR range (6.5-8.5) for discharge water (EGASPIN, 2018). The oil and grease is removed in the dissolved air floatation sub-unit in the refinery. The sub-unit is designed to remove oil and suspended solids by dissolving air under pressure in the wastewater and oil which are routed from oily pond, tank drains, equipment oil leaks and ballast water tanks. The resultant air bubbles cleave to the oily particles and suspended solids such as sand, silt, sediment, plankton and algae and float to the surface and are skimmed as scum to the sludge basin for further treatment while the treated water is routed to the OBSP for discharge to the environment (Moga et al, 2017).

In Feb, there was a decrease in the oil and grease means from 1.87 at RWBD to 1.24 at TWBD as shown in Table 2. There was a very conspicuous reduction in the mean values of the parameter from 2.62 to 0.92 at RWD and TWD sub-units respectively. The drastic reduction of oil and grease in TWD showed the effectiveness in the coagulation, flocculation and skimming processes in the DAF sub-unit.

The functionality of the biodisk and DAF sub-units was shown in the lower values of oil and grease in the OBSP that takes suction of treated water from the units. In July, the oil and grease means ranged from 0.36 to 1.05 in TWBD and RWBD respectively as shown in Table 2. As observed in Feb, the oil and grease values reduced in TWBD relative to the higher value in RWBD. The effectiveness of the DAF sub-unit was also noticed in the reduction of oil and grease mean values from 2.14 at RWD to 0.83 at TWD sub-units before the treated water is delivered to the OBSP as shown in Table 2.

Mean oil and grease values did not vary much between the dry (Feb) and rainy season (July) except for RWD with values of 2.62 and 2.14 respectively. It was observed that the performance of the DAF sub-unit was enhanced due to the evaporation of the volatile hydrocarbons in the dry and rainy seasons with the degree of treatment of 64.9% and 61.2% between the RWD and TWD mean values respectively as shown in Table 2.

The higher value of oil and grease at RWBD in Feb may be attributed to the inability of the microorganisms to effectively biodegrade all the oil and grease since that was not their target material. The OBSP had mean values of 0.79 and 0.46 for Feb and July respectively. These values are within DPR oil and grease specification (Table 2) for discharge into the environment.

Phenolic compounds are present in petroleum products, especially because of the cracking process that occurs in fluid catalytic cracking unit (FCCU), where the high phenolic pool leads to catalyst poisoning (Thuan, et al, 2017). The phenolic compounds are mostly abundant in the process sour water and chemical wastewater and these two serve as influents to the biological treatment sub-unit (RWBD), where phenols are removed to meet DPR standard for discharge into the environment.

The phenol mean values in Table 3, showing a reduction from 43.51 in RWBD to 10.47 in TWBD, translates to 75.94% removal and suggests a reduction of phenolic compounds by the microorganisms in the RWBD sub-unit. The degree of treatment shows the efficiency of the biological treatment sub-unit, which functions chiefly to biodegrade the phenols in refinery process water and reduce them to 0.5ppm or below before sending it to OBSP (EGASPIN, 2018).

The OBSP mean of 11.53 may have been caused by the accumulation of treated water in the TWBD sub-unit prior to week 1-4. Phenol means in July ranged from 1.97 to 22.73 in TWBD and RWBD sub-units respectively, as shown in Table 3. This translates to 91.33% reduction in phenols by the microorganisms in the RWBD sub-unit. This is also a reflection of the effectiveness of the microbial treatment of phenols in the raw water from the refinery process units.

This increased phenol removal in the rainy season (July) may be associated with its high solubility in water, and the influents to the bio-treatment sub-unit in the rainy season accommodate more water. This situation is likely to promote growth of the microorganisms and provide a more convenient medium for microbial activity and consequent biodegradation of the phenolic compounds in the sub-unit (Clyde, 2018). The higher values in weeks 2 and 1 in Feb and July respectively were attributed to the operational fault which led to inability to regulate the process water flow from the fluid catalytic unit to the RWBD sub-unit.

The phenol means of 11.53 and 1.94 at the OBSP sub-unit in Feb and July respectively failed to meet the DPR specification of 0.5ppm for discharge to the environment. Due to these high values, the discharges were batched to ensure that it met specification before its discharge to the environment

Table 1: pH for Biological, DAF Sub-Units and OBSP in Feb and July, 2018

SAMPLE	WEEKS										EFFICIENCY %	
	1		2		3		4		FEB	JULY	FEB	JULY
	FEB	JULY	FEB	JULY	FEB	JULY	FEB	JULY	Mean± SD	Mean± SD		
RWBD	15.8	88	104	0.68	28.62	0.82	26	1.4	43.61± 40.64	22.73± 43.52		
TWBD	10.2	6.5	28.1	0.24	0.7	0.5	2.86	0.65	10.4±1 2.447	1.97±3. 02	75.99	91.33
OBSP	9.97	6.21	28.25	0.22	5.27	0.7	2.64	0.63	11.5±1 1.553	1.94±2. 85		

Table 2: Oil and Grease (ppm) for Biological, DAF Sub-Units and OBSP in Feb. and July, 2018

SAMPLE	WEEKS								MEAN±SD	
	1		2		3		4		FEB	JULY
	FEB	JULY	FEB	JULY	FEB	JULY	FEB	JULY		
RWBD	7.04	9.28	8.42	7.93	7.63	7.87	8.58	7.53	7.92±0.72	8.15±0.77
TWBD	7.58	7.48	7.09	8.63	6.89	8.02	8.13	6.9	7.42±0.55	7.76±0.74
RWD	7.04	9.06	8.49	7.98	7.22	8.2	7.45	7.79	7.55±0.65	8.26±0.56
TWD	7.08	9.29	8.22	8.01	7.24	7.76	7.12	7.76	7.42±0.54	8.21±0.73
OBSP	8.41	8.72	7.17	7.36	7.43	7.18	8.6	7.64	7.90±0.71	7.73±0.69

Table 3: Phenols (ppm) in Biological and OBSP Sub-Units in Feb. and July, 2018

SAMPLE	WEEKS								MEAN		EFFICIENCY %	
	1		2		3		4		FEB	JULY	FEB	JULY
	FEB	JULY	FEB	JULY	FEB	JULY	FEB	JULY				
RWBD	1.89	1.05	1.07	1.34	2.17	0.97	2.36	0.85	1.87± 0.57	1.05± 0.21		
TWBD	1.66	0.25	0.98	0.5	1.02	0.5	1.28	0.19	1.24± 0.31	0.36± 0.16	33.69	65.71
RWD	2.45	3.56	2.16	2.2	3.45	1.75	2.42	1.05	2.62± 0.57	2.14± 1.06		

TWD	0.8	1.5	<0.5	0.82	0.95	0.5	1.02	0.5	0.92±0.11	0.83±0.47	64.88	61.21
OBSP	0.97	0.48	0.11	0.39	0.96	0.5	1.13	0.47	0.79±0.46	0.46±0.05		

Large volumes of refinery wastewater contain sulphides between 60-80mg/L (Dermentzis, 2016). The sulphur in crude oil and petroleum products is an impurity; it is responsible for the production of hydrogen sulphide as a by-product in the refinery (Torres, 2018). The biological treatment sub-unit is designed to biodegrade this odorous inorganic compound bearing in mind its allowable limit by DPR.

The sulphide means in Feb as shown in Table 4 decreased from 4.18 at RWBD to 0.06 at TWBD, suggesting a 98.56% reduction of hydrogen sulphide by the microorganisms in the RWBD sub-unit. A similar reduction in the mean values is observed in the sulphide mean from 3.80 in RWD to 0.12 in TWD. The degree of desulphurization by microbial activity (98.56%) in the biological treatment sub-unit is approximately the same as in the dissolved air floatation sub-unit (96.84%). The efficiencies of the biodisks and the DAF sub-units are reflected in the lower sulphide values (Table 4) of OBSP, which receives treated water from the units. The values in OPCH sub-unit (Table 4) are even lower than those in OBSP (Table 4) indicating that there was no ingress of hydrogen sulphide into the drainage system.

Sulphide means in July ranged from 0.08 in OPCH to 7.48 in RWBD sub-units (Table 4). The degrees of sulphide removal in the biological treatment and the DAF sub-units are 98.66 and 98.74% respectively. The lower values of TWBD and TWD (Table 4) show the effectiveness of the biodisk and the DAF sub-units. The mean sulphide values varied remarkably between the dry (Feb) and rainy season (July) as observed in RWBD, with values of 4.18 and 7.48 respectively. The difference in these values cannot be explained by temperature variation alone, being 26.75 and 26.25^{o}C for Feb and July respectively.

Table 4: Sulphide (ppm) in Biological, DAF, OBSP, and OPCH Sub-Units in Feb. and July, 2018

SAMPLE	WEEKS								MEAN		EFFICIENCY %	
	1		2		3		4		FEB	JULY	FEB	JULY
	FEB	JULY	FEB	JULY	FEB	JULY	FEB	JULY				
RWBD	4.78	8.64	4.12	9.55	3.56	4.41	4.24	7.33	4.18±0.50	7.48±2.24		
TWBD	0.08	0.05	0.05	0.06	0.05	0.13	0.07	0.16	0.06±0.02	0.10±0.05	98.56	98.66
RWD	3.38	8.15	0.04	6.1	5.23	9.5	6.55	4.86	3.80±2.82	7.15±2.07		
TWD	0.17	0.07	<0.05	0.12	0.11	0.09	0.09	0.09	0.12±0.04	0.09±0.02	96.84	98.74
OBSP	0.09	0.06	0.05	0.1	0.06	0.09	0.07	0.14	0.07±0.02	0.10±0.03		
OPCH	<0.05	0.06	<0.05	0.12	<0.05	0.08	<0.05	0.04	<0.05±0	0.08±0.03		

The elevation of sulphides at RWBD in July may be attributed to the reduction of microbial concentration of their sub-units, caused by heavy rains blowing off the content of the units. It was also observed that the values of OPCH (Table 5) increased relatively in July. The excess may be attributed to increase in dissolved sulphur gases brought down from the atmosphere into runoff as acid rain (Samantha et al, 2017). The mean values of OBSP (0.07 in Feb and 0.10 in July) are within the DPR tolerance limits (Table X) before it discharges into the environment.

Chromium mean values in Feb ranged from <0.01 in TWD to 0.02 in RWBD sub-units (Table 5). There was a reduction in the mean values from 0.02ppm at RWBD to 0.01ppm at TWBD sub-units. This equates to a removal efficiency of 50% by microbial activity in the biological

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treatment sub-unit. It was observed that the reduction was more in the DAF sub-unit, decreasing from 0.02ppm at RWD to <0.01ppm at TWD sub-units. This may be attributable to the efficiency of the coagulation, flocculation and skimming processes at the DAF sub-unit in expunging most solid materials and transferring them to the sludge basin for further treatment.

The heavy metal means ranged from <0.01 at TWD to 0.01 at RWBD, TWD, OBSP and OPCH sub-units in July. The microbial activity in the biological treatment sub-unit did not make any impact on the influent at RWBD and TWBD as shown in the mean, 0.01ppm in the sub-units before the raw water was sent to the OBSP. This may be attributed to the reduction of microbial concentration of the sub-units caused by heavy rains blowing off the content of the units. A significant reduction was observed in the DAF sub-unit as shown in Table 5. The mean 0.01 decreased to <0.01 in TWD, portraying the efficiency of the DAF sub-unit in removing solid particles from the wastewater influent from the oily pond.

Mean chromium values did not vary much between the dry (Feb) and rainy season (July) except for RWBD with values of 0.02ppm and 0.01 respectively showing a variation of 50.0% between the two seasons. The chromium mean values of 0.01ppm in the two seasons may be showing the presence of the metal in the refinery soil that is conveyed through runoff to the OPCH sub-unit.

The chromium mean values were slightly lower in the rainy season (July) as shown in Table 5. This may be attributed to the solubility of some chromium compounds which are soluble only at high temperatures (Sharon, et al, 2012) and the observed temperatures in Feb and July were 26.75 and 26.25^{0}C respectively. Since the temperatures in the Feb and July were comparable, the lower values in July may also be attributable to the dilution of the chromium metals by the rainwater. The mean values of OBSP (0.01ppm in Feb and July) is within the DPR tolerance limit of 0.05ppm for discharge into the environment

Table 5: Chromium (ppm) in Biological, DAF, OBSP and OPCH Sub-Units in Feb. and July, 2018

SAMPLE	WEEKS								MEAN		EFFICIENCY %	
	1		2		3		4		FEB	JULY	FEB	JULY
	FEB	JULY	FEB	JULY	FEB	JULY	FEB	JULY				
RWBD	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.02±0.00	0.01±0.00		
TWBD	0.01	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01±0.00	0.01±0.00	50	
RWD	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.02±0.00	0.01±0.00		
TWD	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01±0.00	<0.01±0.00	100	
OBSP	0.01	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01±0.00	0.01±0.00		
OPCH	0.01	0.01	0.01	0.01	0.01	0.01	0.08	0.01	0.03±0.04	0.01±0.00		

The biological treatment and the DAF sub-units were available to remove lead, a heavy and toxic metal from the refinery wastewater but as shown in Table 6, the metal was not detected in RWBD, TWBD, RWD, TWD and OBSP. However it was observed that the OPCH sub-unit had the mean value of 0.01ppm in the dry season of February and rainy season of July, which is attributable to the presence of lead in the soil that is washed into the runoff. The observed value is far below the DPR limit of 0.05ppm for discharge to the environment and corroborates reports that lead has the lowest concentration (Ni > V > Cd > Pb) in Bonny light crude, the feedstock to the Port Harcourt refinery, ranging from 0.200 to 0.01ppm (Wilberforce, 2016)

The non-detectability of lead in the wastewater may also be attributed to the abolition of the application of tetraethyl lead (TEL) as octane booster to blend Premium Motor Spirit (PMS) for internal combustion engines after the advent of Fluid Catalytic Cracking and Reforming Units that produce gasoline of very high octane number (Abhishek,. et al, 2018). Lead was not detected in

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the OBSP in Feb and July, thereby meeting the DPR specification of 0.05ppm for discharge into the environment

Table 1.6: Lead (ppm) in Biological, DAF, OBSP and OPCH Sub-Units in Feb. and July, 2018

SAMPLE	WEEKS								MEAN	
	1		2		3		4		FEB	JULY
	FEB	JULY	FEB	JULY	FEB	JULY	FEB	JULY		
RWBD	0.01	<0.01	0.01	<0.01	0.01	<0.01	0.01	<0.01	0.01±0.00	<0.01±0.00
TWBD	<0.01	<0.01	0.01	<0.01	0.01	<0.01	0.01	<0.01	0.01±0.00	<0.01±0.00
RWD	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01±0.00	<0.01±0.00
TWD	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01±0.00	<0.01±0.00
OBSP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.01±0.00	<0.01±0.00
OPCH	0.01	0.01	0.01	0.01	0.01	0.01	<0.01	0.01	0.01±0.00	0.01±0.00

Copper mean values in July ranged from 0.01ppm in TWBD, RWD, OBSP and OPCH to 0.02ppm in RWBD sub-units (Table 7). As observed in Feb, the copper values (Table 7) in RWBD were reduced compared to the values in TWBD. The reduction from 0.02 to 0.01ppm at RWBD and TWBD respectively due to the microbial activity translates to 50% efficiency. This is also a reflection of the effectiveness of the microbial treatment of the raw water from the refinery process units

The Feb copper means ranged from 0.01 at TWD to 0.20ppm at RWBD. There was reduction in Feb copper means in Table 8 from 0.20 at the RWBD to 0.16ppm at TWBD sub-units. This translates to a removal efficiency of 2.0% only by microbial activity in the biological treatment sub-unit. Similarly, the DAF sub-unit showed a reduction of the mean values from 0.15 at the RWD to 0.01ppm at TWD sub-units, an efficiency of 93.3%. The lower efficiency in the biodisk is attributable to the findings that copper is toxic to microorganisms by interfering with the electrical charges of their cell membranes (Erica, 2020). The efficiencies of the biodisks and the DAF sub-units are reflected in the lower copper values of OBSP (0.02ppm) which receives treated water from the units.

A similar observation can be made between the higher values of copper in RWD and the lower values of TWD, which has higher copper than TWD as shown in Table 1.8. As observed in Feb, the treatment efficiency for July is also higher (93.33%) in the DAF sub-unit, as copper is not detectable at all in the TWD.

Mean copper values varied between the dry (Feb) and rainy season (July) for RWBD with values of 0.20 and 0.02 respectively, which translates to 90% difference.

The observed higher mean copper value may be attributed to the solubility of copper sulphate, a probable compound in refinery wastewater due to copper and abundant sulphuric acid solutions and its sensitivity to slight temperature change on the microbial activity, even though the observed temperatures in the Feb and July were about the same at 26.75 and 26.25^{0}C respectively (Heather, et al, 2011). The mean values of OPCH were also slightly higher in Feb.

The copper mean values of OBSP, 0.03ppm and 0.01ppm in the dry (Feb) and rainy (July) season respectively were below the DPR specification of 1.5ppm for discharge into the environment.

The Feb zinc means in Table 1.8 showing a reduction from 0.15 in RWBD to 0.13ppm in TWBD, translates to 13.3% and suggests a reduction of the metallic element by the microorganisms in the RWBD sub-unit. A similar reduction in the mean values is observed from 0.15 in RWD to 0.01 in TWD- a 93.3% removal efficiency in the DAF sub-unit. This higher efficiency of zinc reduction in the DAF sub-unit is attributable to the efficiency of the floatation treatment of the raw water entering RWD sub-unit from the oil separation pond, in that the dissolved and suspended solids were successfully coagulated, floated to the surface and skimmed off before underlying water was allowed to flow into the TWD sub-unit

The efficiencies of the biodisks and the DAF sub-units are reflected in the lower zinc values (0.01ppm) of OBSP which receives treated water from the units.

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Table 7: Copper (ppm) in Biological, DAF, OBSP and OPCH Sub-Units in Feb and July, 2018

SAMPLE	WEEKS								MEAN		EFFICIENCY %	
	1		2		3		4		FEB	JULY	FEB	JULY
	FEB	JULY	FEB	JULY	FEB	JULY	FEB	JULY				
RWBD	0.3	0.02	0.1	0.02	0.2	0.01	0.2	0.01	0.20±0.08	0.02±0.01		
TWBD	0.2	0.01	0.1	0.01	0.2	0.01	0.14	0.01	0.16±0.05	0.01±0.00	20	50
RWD	0.2	0.01	0.1	0.01	0.2	0.01	0.11	0.01	0.15±0.06	0.01±0.00		
TWD	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01±0.00	0.01±0.00`	93.3	0
OBSP	<0.01	<0.01	0.01	0.01	0.01	0.01	0.08	0.01	0.03±0.04	0.01±0.00		
OPCH	0.01	0.01	0.01	0.01	0.01	0.01	0.04	0.01	0.02±0.02	0.01±0.00		

Table 8: Zinc (ppm) in Biological, DAF, OBSP and OPCH Sub-Units in Feb. and July, 2018

SAMPLE	WEEKS								MEAN		EFFICIENCY %	
	FEB	JULY	FEB	JULY	FEB	JULY	FEB	JULY				
RWBD	0.1	0.02	0.16	0.02	0.1	0.02	0.25	0.02	0.15± 0.07	0.02± 0.00		
TWBD	0.1	0.001	0.1	0.01	0.1	0.02	0.21	0.013	0.13± 0.06	0.01± 0.01	13.33	50
RWD	0.1	0.01	0.2	0.01	0.1	0.01	0.2	0.01	0.15± 0.06	0.01± 0.00		
TWD	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01± 0.00	0.01± 0.00	93.33	0
OBSP	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01± 0.01	0.01± 0.00		
OPCH	0.01	0.01	0.01	0.01	0.01	0.01	0.09	0.01	0.03± 0.04	0.01± 0.00		

Zinc means in July ranged from 0.01ppm in RWBD, TWBD, TWD, OBSP, OPCH to 0.04 in RWD sub-units (Table 8). As observed in Feb, the zinc values in the biodisk in July were also reduced

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after microbial activity from 0.02 at RWBD to 0.01ppm at TWBD. This equates to an efficiency of 50% in the sub-unit, as shown in Table 8. Similarly, there was a reduction in the mean values from 0.04 at RWD and to non-detectable at TWD , showing a higher zinc removal efficiency in July at the DAF sub-unit, compared to Feb. This is also a reflection of the effectiveness of the DAF sub-unit in removing metals using the floatation technique in carrying the materials along with the air bubbles to the surface before letting the underlying water to flow to the TWD sub-unit for onward delivery to the OBSP.

Zinc values varied between the dry (Feb) and rainy season (July) for RWBD and RWD with mean values of 0.15ppm and 0.04ppm respectively- a difference of 73.3%. The mean value of OPCH in Feb and July was 0.01ppm showing that the runoff was not overwhelmed by the refinery untreated wastewater.

From the findings of Reddy et al (1995), the observed lower mean zinc value may be attributed to the influence of pH on the solubility and ionization of zinc as the observed pH in the Feb and July were at 7.42 and 8.21 respectively. The mean value of 0.01ppm recorded for OBSP in Feb and in July are within the DPR tolerance limit of 1.0ppm for discharge of zinc into the environment The Feb iron means ranged from 0.01ppm at OBSP and TWD to 0.38ppm at RWBD. The means in Table 9 shows a reduction from 0.38 in RWBD to 0.25ppm in TWBD, translating to 34.2% efficiency and suggesting a reduction of the heavy metal by the microbial activity in the bio-treatment sub-unit. A reduction is also observed in the iron mean values from 0.09 to 0.01ppm in RWD and TWD respectively, equating to 88.9% removal efficiency in the DAF sub-unit. The higher efficiency of iron reduction in the DAF sub-unit is attributable to the efficiency of the floatation treatment of the raw water entering RWD sub-unit from the oil separation pond, in that the dissolved and suspended solids were successfully coagulated, floated to the surface and skimmed off before underlying water was allowed to flow into the TWD sub-unit.

The iron means in July ranged from 0.01ppm in TWD and OPCH to 0.04ppm in RWBD sub-units, as shown in Table 9. As observed in Feb, the iron values in the biodisk were also reduced after microbial activity at RWBD from 0.04 to 0.02ppm at TWBD. This is equivalent to an efficiency of 50% in the sub-unit (Table 1.10). Similarly, there was a reduction in the mean values from 0.03 at RWD to 0.01ppm at TWD, showing a higher iron removal efficiency of 66.9% in the DAF sub-unit, as was also observed in Feb. This is also a reflection of the effectiveness of the DAF sub-unit in removing metals using the floatation technique in carrying the materials along with the air bubbles to the surface before letting the underlying water to flow to the TWD sub-unit for onward delivery to the OBSP.

There was a variation of 89.5% between the iron mean values between the dry (Feb) and rainy season (July) at RWBD values of 0.38ppm and 0.04ppm respectively. The mean value of 0.01ppm at OPCH in Feb and July may be a reflection of the iron concentration of the soil at the sampling periods.

The observed iron mean values of the OBSP at 0.05ppm and 0.03ppm in Feb and July respectively were within the DPR specification of 1.0ppm for discharge into the environment.

Table 9: Iron (ppm) in Biological, DAF, OBSP and OPCH Sub-Units in Feb. and July, 2018

SAMPLE	MONTHS								MEAN		EFFICIENCY %	
	FEB	JULY	FEB	JULY	FEB	JULY	FEB	JULY			FEB	JULY
RWBD	0.1	0.02	0.16	0.02	0.1	0.02	0.25	0.02	0.15±0.07	0.02±0.00		
TWBD	0.1	0.001	0.1	0.01	0.1	0.02	0.21	0.013	0.13±0.06	0.01±0.01	13.33	50
RWD	0.1	0.01	0.2	0.01	0.1	0.01	0.2	0.01	0.15±0.06	0.01±0.00		
TWD	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01±0.00	0.01±0.00	93.33	0
OBSP	0.0	0.01	0.0	0.01	0.0	0.01	0.0	0.01	0.01±0.0	0.01±0.0		

	1		1		1		2		1	0
OPC H	0.0 1	0.01	0.0 1	0.01	0.0 1	0.01	0.0 9	0.01	0.03±0.0 4	0.01±0.0 0

Table X: DPR Standards for Discarge Limitations for Treated Petroleum Refinery Waste Water

S/N	Effluent Characteristics	**Compliance Limits: Maximum for Any One (1) Day Period**
1	$BOD_{5,}$ mg/L	10
2	COD, mg/L	40
3	Total Dissolved Solids (TDS) mg/L	<2000
4	Total Suspended Solids (TSS) mg/L	30
5	Total Hydrocarbon Content (THC) mg/L	10
6	pH	6.5-8.5
7	Temperature, ^{0}C	Ambient ± 2
8	Sulphide as H_2S, mg/L	0.1
9	Ammonia (NH_4), mg/L	1.5
10	Phenols (Total), mg/L	0.5
11	Cyanide, mg/L	0.07
12	Total Chromium, mg/L	0.05
13	Pb^{2} mg/L	0.05
14	Total Iron (Fe), mg/L	1.0
15	Cu^{2+}, mg/L	1.5
16	$Zn^{2=}$, mg/L	1.0

(Source: EGASPIN, 2018**)**

III. CONCLUSION

The pH values of the liquid effluents were basic with the mean values of 7.42-8.26 for the two seasons and within the range for optimum microbiological treatment effectiveness. The efficiencies of pollutants removal in effluent water in the biological treatment and the dissolved air floatation sub-units of the refinery were calculated. The pollutants such as oil and grease, phenols, phosphates, sulphides and the metal ions were drastically reduced in the treated water biodisk and the dissolved air floatation treatment sub-units. The efficiency of removal of sulphides from the influents of the sub-units was optimally high to reduce their negative impacts in the environment and the refinery catalysts.

The presence of metal ions in the refinery effluent water was very minimal with lead showing the least values. This was attributable to the absence of tetra ethyl lead which was formerly used as octane number boosters in the refinery. The advent of the secondary units like catalytic reforming and catalytic cracking units has led to the massive production of fuels with very high octane number that are used as blend stocks for premium motor spirit (PMS) popularly called, petrol.

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