Effluent Waste Management In A Nigerian Refinery

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***Abstract*—Industrial wastes are solids, liquids or gaseous products in treated or untreated conditions discharged from a process where each of such effluents contain a number of potentially polluting chemical substances. Effluent water sample from a refinery in Nigeria was treated and both were tested for compliance with the Federal Environmental Protection Agency's effluent limitations. Treated effluent waste quality parameters complied with the limitations but phenol concentration did not comply due to the fact that the treatment process is not 100% efficient. The temperature of the effluent water could have been reduced by allowing more retention time in the observatory pond prior to discharge.**

Keywords—environment, refinery, petroleum, pollution, waste.

I. INTRODUCTION

It is commonly noted that the issue of environmental hazard is mostly and popularly traced to pollution problems. These problems ranges from solid waste, sewage water, air pollution and water pollution. The three categories of pollution are noise pollution, air pollution and water pollution [1].

Water pollution is described as the presence in a stream of an excessive amount of a specific pollutant or pollutants [2].

Waste water can be either domestic or industrial type [3]. Industrial waste is identified as any solid, liquid or gaseous product in treated or untreated condition that is discharged from a process where each of such effluents contained a number of potentially polluting chemical substances [4]. The origin of waste water treatment started in the early 1200s when irrigation and intermitted filtration methods were used for treatment. As years roll by, treatment objectives increases with an increased understanding of the environmental effects caused by waste water discharges, a developing knowledge of the adverse long term effects caused by the discharge of some specific constituents waste water and the development of national concern for environmental protection [5]. Therefore, treatment objectives must go hand-in-hand with the water quality objectives or standard established by the federal, state, and regional regulatory authorities.

1.1 Classification of Waste Water Treatment Methods

After treatment objectives have been established and the applicable state and federal regulations have been reviews, then the degree of treatment can be determined by comparing the influent waste water characteristics to the required effluent waste water characteristics, the contaminants in waste water are removed by physical chemical and biological processes.

Processes involved in conventional waste water include: pre-treatment, secondary treatment, tertiary and sludge disposal.

1.1.1 Pre- and Primary Treatment

Pretreatment processes are those operation used be screen out coarse solids, to reduce the size of solids, to separate floating oils and to equalize fluctuation in flow. Primary treatment usually refers to the removal of suspended solids by settling or floating. The treatment methods involve the application of physical forces and are therefore called physical unit operations:

Typical unit operations include screening, mixing, flocculation, sedimentation, flotation and gas transfer. Gravity - type separator or the API separator is used in the refinery to separate oil wastes. Sedimentation operation is the most widely used physical unit operation. Solids in particular are allowed to settle to the bottom of a tank under quiescent condition, chemicals may also be added for chemical coagulation and separation of suspended solid particles. Primary reduction of solids reduces oxygen requirement in a subsequent biological step and also reduces the solid loading of secondary sedimentation tank.

1.1.2 Secondary Treatment

This invokes a biological process to remove organic matter through biochemical oxidation. The particular biological process selected depends upon such factors as quantity of waste water, biodegradability of waste and availability of land. The most commonly used being activated sludge reactors, Rotary biological contractors and tricking filters. In the activated sludge, waste water is fed into and treated tank where microorganisms consume organic wastes for maintenance and for generation of new cells. The resulting microbial flow (activated sludge) is settled in a sedimentation vessel called a clarifier.

1.1.3 Tertiary Treatment

In order to remove particular contaminates and prepare the waste water for reuse tertiary treatment is required. This involves the removal of phosphorous compound by coagulation with chemicals, removal of nitrogenous compound by ammonia stripping with air (nitrification — denitification in biological reactors), removal of residual organic and colour compounds by adsorption on activated carbon and removal of dissolved solids by membrane processes (reverse osmosis and electro dialyses). The effluent water is often treated with chlorine or ozone to destroy pathogenic organisms before discharge into the receiving waters.

1.1.4 Sludge Disposal

The sludge or solid deposit generated from waste water treatment processes are treated by common sludge treatment sequences. Concentration operations, such as gravity or flotation thickeners increase the solids concentration and achieve a significant reduction in sludge volume while stabilization operations such as anaerobic digestion convert sludge into a less offensive form in terms of odor, degradability and pathogenic content. Other operations include chemical addition and heat treatment to improve dewatering rate; Dewatering to reduce volume; incineration and heat drying to dry sludge cake. Finally, ultimate disposal of sludge solids by land fill, spreading on soil, lagoons and ocean.

TABLE 1: UNIT OPERATIONS AND PROCESSES AND WASTE WATER TREATMENT SYSTEMS USED TO REMOVE MAJOR CONTAMINANTS FOUND IN WASTE WATER

Contaminant	Unit operation, unit process or treatment system
Suspended solids	Screening and communition Grit removal, sedimentation, filtration, flotation, coagulation/ sedimentation
Biodegradable organic	Activated sludge, trickling filterers, lagoons or pond and rotary Bio Disk
Volatile organic	Air stripping, off gas treatment, carbon adsorption
Pathogens	Chlorination, ozonation and UV radiation.
Phosphorous and nitrogen	Metal salt addition, lime coagulation / sedimentation biological nutrient removal
Heavy metals	Chemical precipitation, ion exchange.
Dissolved organic solid	Ion exchange, reverse osmosis

2. PROCEDURE/ANALYSIS

2.1 Determination of the Effluent Waste Water Quality Parameters

2.1.1 Method for Determination of the Suspended Solids

Solids in waste water are classified as settleable solids and non-settleable solids. Settleable solids are removed by primary sedimentation. Non-settleable or total solids are all the matter that will remain as residue after evaporation at 103 or 105°c. The total solids are comprised of non-filterable or suspended solid and filterable or dissolved solids. The apparatus required for the solid test are oven, dessicator, glass fibre filter and a chemical balance.

A glass fibre filter paper was dried at 180°C for 2 hours, cooled to room temperature in a dessicator and then weighted. The glass fibre filter was placed in a filter funnel and attached to a conical flask. A thoroughly mixed sample was measured at 100ml and filtered through the above set up, taking care not to spill any. The residue was removed and dried in the oven at 180°C. The dried residual was then cooled in the dessicator and weighted in the chemical balance.

2.1.1.1 Process Control Calculation for Suspended Soli

$$T_s = \frac{M_{er} - M_e}{L} * 1000mg/g \qquad (1)$$

Where, T_s = Total Solid, (mg/L)
M_{er} = mass of evaporating dish plus residue
M_e = mass of evaporating dish
L = sample size

$$T_{ss} = \frac{R_{gf} - T_{gf}}{L} * 1000mg/g \qquad (2)$$

where, T_{ss} = Total Suspended Solid, (mg/L)
R_{gf} = residue on glass fibre filter after drying at 105^0C
T_{gf} = total mass of filter glass fibre

2.1.2 Method for Determining the pH of the Effluent Waste Water

pH is a measure of hydrogen ion concentration. It is defined as the negative logarithm of the hydrogen ion concentration. pH = - log (H^+)

There is need to maintain the pH of influence and effluent waste water at a permissible range suitable for existence of biological life use in the biological treatment and aquatic life in the receiving water bodies.

The concentration range suitable for the existence of most biological life is quite narrow and critical.

The pH values are determined by the use of a pH meter. The pH meter was calibrated by a buffer standard solution. A buffer solution of pH value of 7 was poured into a clean beaker and the temperature measured by the use of a thermometer inserted into the beaker.

The buffer was thoroughly mixed with a magnetic stirrer and the pH meter was adjusted to road the pH value. The process was repeated with a standard buffer solution of pH value of 10 and the pH meter was now calibrated.

The sample of the waste water was then measured into a clean beaker, stirred with the magnetic stirrer and placed in the pH meter to record the pH value.

2.1.3 Method for Determination of the Biochemical Oxygen Demand (BODs)

The laboratory methods commonly used to measure gross amount of organic matter (greater than 1 mg/L) include the:

- Biochemical oxygen demand
- Chemical oxygen demand (COD)

The BOD test, though not without limitations, is used to determine the following.

- The approximate quantity of oxygen that will be required to biologically stabilize the organic matter present in the waste water.
- The size of waste water treatment facilities.
- The efficiency of waste water treatment processes
- Compliance of effluent waste water with waste water discharge permits.

The BOD test is carried out with a BOD analyzer in the laboratory.

A sample suitably diluted with specially prepared dilution water was incubated in an incubator for five days period to give the BOD5.

The specially prepared dilution water may be seeded with a bacteria culture or not depending on the population of microorganism present in the waste water sample. The BOD bottles were filled with 300ml of the sample and placed in the BOD controller model 606T. The bottles were stoppered with a rubber bung and a pellet of sodium hydroxide. The apparatus was then switched on and the reading taken on the fifth day at a constant temperature of 20°C was taken as the BOD5 value.

The procedure for setting up a BOD5 is illustrated in Fig 1.

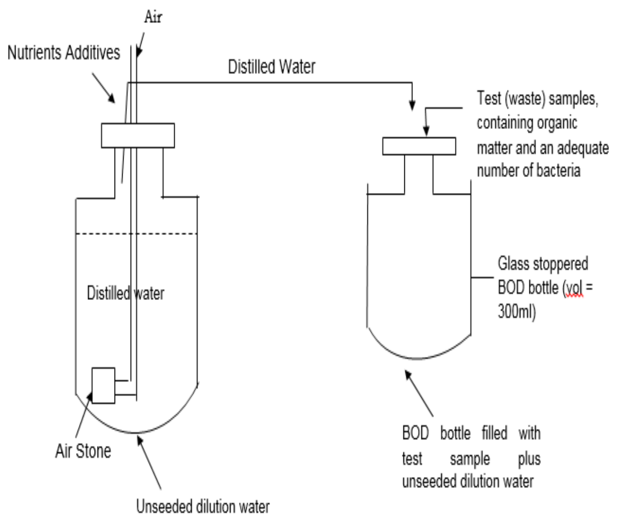

Fig 1: Procedure for Setting up BOD5 Test

2.1.3.1: Process Control Calculations for BOD Test

$$BOD, \frac{mg}{L} = \frac{D_1 - D_2}{P}$$ (when dilution water is unseeded) (3)

$$BOD, \frac{mg}{L} = \frac{(D_1 - D_2) - (B_1 - B_2)F}{P}$$ (when dilution water is seeded) (4)

$$Y_t = L - Lt(1 - e^{-kt}) \quad (5)$$

$$Y_5 = L - L_5(1 - e^{-5t}) \quad (6)$$

Where

D_1 = dissolved oxygen of diluted sample after 5 day incubation at 20°C, mg/L

P = decimal volumetric fraction of sample used.

F = ratio of seed in sample to seed in control = (% seed in Di) / (% seed in B_1)

B_1 = dissolved oxygen of seed control before incubation, mg/L

B_2 dissolved oxygen of seed control after incubation, mg/L

L = the total or ultimate first stage BOD initially present at time, t=0

L_t = the amount of BOD remaining at time t

Y_t = the amount of BOD that has been exerted at any time t_y

Y_5 = the 5-day BOD value, BODs

K = the reaction rate constant ranging from 0.05 to 0.3d -1

2.1.4 Determination of the Chemical Oxygen Demand (COD)

COD is test is also used to measure the content of organic matter of waste water. The test gives the oxygen equivalent of the organic matter that can be oxidized using a strong chemical oxidizing agent in an acidic medium. It improves the limitations of BOD test by measuring non-biodegradable organic matters in an industrial waste that contain compound which are toxic to biological life. The COD of a waste is in general higher than BOD because more compounds can be chemically oxidized than can be biologically oxidized.

Chemical oxygen demand vials or containers are used for the test. About 2mls of waste sample was piped into each of the labeled vials and cooled under tap water. The vials were put inside chemical oxygen demand reactor and digested at 150°C for 2hours. After cooling, the concentrations were read off from spectrophotometer at 620mm wave length using the control vial as standard.

The principal reaction using dichromate as the oxidizing agent can be represented in a general way by the following unbalanced equation

Organic matter (C_aH_bO) + $Cr_2O_7^{-2}$ + H^+ $\xrightarrow[\text{Heat}]{\text{Catalyst}}$ Cr^{+3} + CO_2 + H_2O.

Other important waste water quality parameter determined include phenol content, oil content, sulphur content, cyanide and chromium contents.

Tables 2 and 3 give the value obtained from testing the influent and effluent waste water quality parameters, conducted in a Nigerian refinery used as the case study for this work.

2.2 Quantitative and Qualitative Appraisal of the Refinery Waste Water Treatment Methods and its Waste Water Quality Parameters

This is highlight of the treatment equipment, the waste water treatment system and sources that generate waste water in the Nigerian Refinery used as the case. Then, followed by quantitative and qualitative appraisal of the treatment processes and the waste water quality parameters.

2.2.1 Treatment Systems and Sources of Waste Water Generation

In the Nigerian refinery used as the case, waste water treatment is carried out in the waste water plant. The plant treatment process is classified into two systems as shown in Fig 2 below.

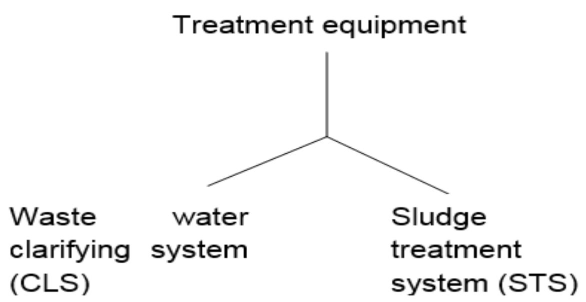

Fig 2: Classification of Refinery Waste Water Treatment System

The waste water clarifying system is further divided into two sections as shown in Fig 3 below.

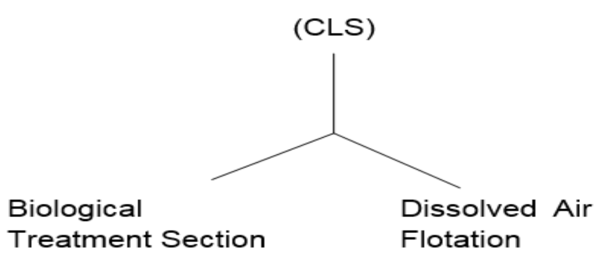

Fig 3: Types of Waste Water Clarifying System

Below is an enumeration of the sources of refinery waste water generation. There are six kinds of waste in this system, which include:

- Process waste water
- Caustic waste water
- Sanitary waste water
- Oily water and oily rain water
- Ballast water
- Dimersol effluent.

Process waste water include water from desalter in crude distillation unit, FCC sour water stripping section and sour water and caustic treatment unit. Pollutants in process water include oil and BOD elements.

Sanitary waste water include water from toilet effluents and kitchen waste water. Their pollutants include mainly BOD elements.

Oily sewer water include rain water which has fallen in possible oil contaminated paved areas, drain water from vessels, pumps and tank. Pollutants in it are oil and suspended solid.

Ballast water is water discharged from oil tankers and ocean going vessels. Pollutants in it are oil and suspended solid.

Chemical waste water is waste from the laboratory and spent caustic water. Laboratory waste water contains oil and suspended solid while spent caustic water contain phenol and BOD elements. Dimersol effluent contains suspended solids only.

There is also the seventh type of waste water which does not require treatment. This is called clean waste water which include boiler blown down and condensate, from process unit. Though these sources generate waste water for treatment, their treatment sections differ with regard to the pollutants they contain.

Process waste water, sanitary waste water, chemical waste water and Dimersol effluent filtrate are treated in the biological section of the waste water clarifying system because they contain BOD elements.

Ballast water and oily sewer water are treated in the dissolved air flotation section (DAF) because of their high content of suspended solid.

2.2.2 Sludge Treatment System

Packaged waste water treatment section is divided into the following sludge handling systems as shown in Fig 4.

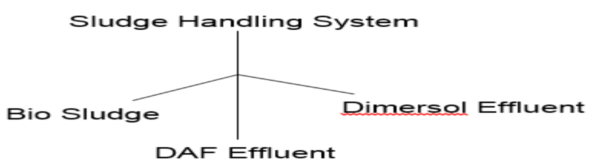

Fig 4: Classification of Sludge Handling System

The sludge removed from biological treatment section is called bio sludge while that removed from DAF treatment section is called DAF sludge. Both bio sludge and DAF sludge from the DAF tank are dewatered and dried by the centrifuge (dehydrator). The dewatered cake is then stored in the cake banker. The bio dewatered cake is fed to the cake hopper through the belt conveyor and then is charged to the rotary kiln for incineration. Bio sludge is incinerated because of the harmful substances it contains. The dimersol sludge is filtered in the press filter and the cake discharged away into the cake banker while the filtrate is returned to bio treatment system.

3. RESULTS

3.1 Quantitative Appraisal of Waste Water Quality Parameters

From Table 3.1, the total quantity of influent waste water is gotten to be 521.6m^{3}/hr.

Converting this to gal/day gives 3307 371.2 gal/day or 3.307 million gal/day. This is a great quantity of waste water to be dealt with. Discharging it untreated into the inland water will cause unimaginable havoc to the aquatic life and also render the surface water use harmful and unsightly. The alternative of treating it will require the design of a sizeable treatment process with its attendant high capital cost. However, the potential havoc this quantity of waste water will cause far out weights the cost of equipment design and treatment operations.

Again looking at the composition of the influent waste water a total phenol content of 2032 mg/L, oil content of 635mg/l, BOD content of 3748 mg/l, COD content of 5600rng/l, presence of a sizeable quantity of cyanide and sulphide will amount to a devastating pollution of the inland water if discharged untreated.

3.2 Qualitative Appraisal of Effluent Quality Parameters

The above quantity of influent waste water is subjected to treatment and the resultant quality parameters are tabulated in Table 3.2. From this result, we can see a considerable reduction of phenol content to 0.05mg/L, BOD5 content to average of 15mg/l, COD content to 150mg/l, TSS content to 5mg/L, and pH of the range of 6-8.5. The plant efficiency for BOD5 and TSS removal is calculated to give 99.6% and 99% respectively. This gives a high efficiency of the treatment plant in reducing the BOD5 and TSS. This result is seen when the refinery effluent waste standards are compared with FEPA effluent limitations. Table 3.2 shows an average BODS of 15mg/L which is slightly consistent with FEPA BOD5 value of 10mg/L (Table 3.3), Table 3.2 TSS of 5mg/L shows a high reduction in value when compared with FEPA TSS value of 30mg/L (Table 3.3). The values of COD, phenol and oil content shown in Table 3.2, as obtained from the refinery effluent contrasted sharply with the EPA effluent limitations values shown in Table 3.3. The high COD of the treated effluent is an indication of the presence of non biodegradable organic and dissolved organic matters. The oil content of the treated effluent indicates inefficient separation of oil from the waste water prior to waste water clarification treatment. Presence of phenol in unacceptable concentration shows ineffectiveness of the treatment process in removal of phenol. The presence of Ammonia indicates that the nitrification stage of the rotary bio disk is absent or inefficient. Temperature of the effluent waste water can be reduced to an acceptable value by allowing more retention time in the observatory pond prior to discharge. The value of the pH is consistent with the FEPA permissible value.

TABLE 2: EFFLUENT WASTE WATER COMPOSITION AS COLLECTED IN A NIGERIAN REFINERY FOR TREATMENT

QTY	PW	SC	SW	OW	BW	CW
m^3/hr	118.9	1.7	15	75	300	11
Properties (mg/L)						
pH	8.5	6 - 8	6 - 8	6 - 8	7 – 8.5	8.5
BOD5	260	3250	118	50	50	20
COD	500	4250	300	200	200	150
Oil	200	200	10	200	20	5
TSS	100	100	100	100	100	5
Phenol	32	2000				
Total Cyanide	28					
Sulphide	10	5				

TABLE 3: TREATED EFFLUENT WASTE QUALITY PARAMETERS FROM A NIGERIAN REFINERY FOR TREATMENT

Property	Effluent Water Concentration
BOD5	10 – 20 mg/L
COD	150 mg/L
pH	6 - 8.5
Phenols	0.05 mg/L
Oil	5 mg/L
Lead	0.1 mg/L
Total Cyanide (cn^-)	1.00 mg/L
Hexa-chromium (Cr^{6+})	0.03 mg/L
Sulphide (S^{2-})	0.1 mg/L
TSS	5 mg/L
Temperature	38^0C
Appearance	Clear

TABLE 4: FEPA EFFLUENT LIMITATIONS GUIDELINES FOR MAXIMUM CONCENTRATION ALLOWED FOR DISCHARGE INTO INLAND WATERS

Effluent Parameters	Discharge Limit for Inland Waters (Fresh Surface Water)
Temperature, ^0C	35
pH	6.5 – 8.5
Oil and Grease	10
TSS	30
BOD5	10
COD	40
Lead (Pb^{2+})	0.05
Chromium (Cr^{6+})	< 0.10
Zinc (Zn^{2+})	1.00
Copper (Cu^{2+})	1.50
Cadmium (Cd^{2+})	< 0.10
Phenol	< 0.01
Sulphur	No Specification

4. CONCLUSION

Water pollution is the cause of the extinction of aquatic life and it renders water unsafe for human consumption. In the Petroleum industry, apart from banker accidents and discharges in Navigation waters, discharges from offshore production facilities, another major source of water pollution is the effluent waste from petroleum refineries. If untreated waste water is allowed to accumulate, the decomposition of organic materials it contains can lead to production of large quantities of malodorous gases. Waste water also contains nutrients, which can stimulate the growth of aquatic plants and it also contains toxic compounds.

For these reasons and more, the immediate and nuisance free removal of waste water from its sources of generation, followed by treatment and disposal, is not only desirable but also necessary in an industrialized society.

Public health and environmental concern are major factors considered in waste water treatment. The major refinery effluent waste water quality parameters include the pH, BOD5, COD, oil and grease content, TSS and phenol content. Consistency of these parameters with the effluent limitations set by FEPA has been the main findings of this work. If adverse environmental impacts are to be avoided and public health is to be promoted, the quality of the treated effluent must be consistent with the waste water discharge standards set by the federal and state laws before being discharged to inland water.

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NOMENCLATURE

API = American Petroleum Institute
BOD = Biochemical Oxygen Demand
B_1 = Dissolved Oxygen of Seed Control before Incubation, mg/L
B_2 = Dissolved Oxygen of Seed Control after Incubation, mg/L
CLS = Waste Water Clarifying System
COD = Chemical Oxygen Demand
D_1 = Dissolved Oxygen of Diluted Sample after 5-Day Incubation at 20°C, mg/L
DAF = Dissolved Air Floatation
F = Ratio of Seed in Sample to Seed in Control = (% seed in Di) / (% seed in B_1)
FEPA = Federal Environmental Protection Agency
g = Gram
gal/day = gallon per day
K = The Reaction Rate Constant Ranging from 0.05 to 0.3d -1
L = Sample Size
L = The Total or Ultimate First Stage BOD Initially Present at Time, t=0
L_t = The Amount of BOD Remaining at Time t
mg/l = Milligram per Litre
ml = Millilitre
mm = Millimetre
m^3 = Cubic Metre
M_e = mass of evaporating dish
M_{er} = mass of evaporating dish plus residue
P = Decimal Volumetric Fraction of Sample Used
R_{gf} = residue on glass fibre filter after drying at 105^0C
STS = Sludge Treatment System
T_{gf} = total mass of filter glass fibre
Ts = Total Solid
Tss = Total Suspended Solid
UV = Ultraviolet
Y_t = The Amount Of BOD that has been Exerted at any Time, t_y
Y_5 = The 5-day BOD value, BOD5
^{0}C = Degree Celsius