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Analysis of Waste Water Treatment in Kaduna Refining and Petrochemicals Corporation (KRPC) (NNPC Kaduna) Nigeria

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ABSTRACT
Scientific data and results have to be accurate, precise and reliable and are subject to ever increasing scrutiny by regulators in industry, the environment and medicine, in validation and also in research and development. Given our numerous environmental problems, the need for accurate, precise and reliable results cannot be overemphasized in environmental pollution control. This research was undertaken by visiting the analytical laboratory involved in environmental pollution control in Nigerian National Petroleum Corporation (NNPC) Kaduna which is known as Kaduna Refining and Petrochemicals (KRPC). Results were taken within a span of three years at different times of the year. End of month results were also taken for the two receiving rivers (River Kaduna & Romi River) and effluent from the refinery. The waste water was analyzed using available instruments in the Refinery such as PH meter, Dissolved Oxygen (DO) Meter, Conductivity Meter, Gas chromatography, burette, pipette, Double beam Spectrometer, and Thermometer. The results showed that many parameters meet the standard of limit set by the Nigerian Standard Organization but there are many vital parameters whose limits are very low but not measured for lack of instruments. The point of concern here becomes the availability of suitable analytical instruments for quality control in the waste water treatment.
Keywords: Environmental, Pollution, Analytical instruments, Waste Water, Petrochemicals

I. INTRODUCTION

Mankind has put thousands of organic compounds to use in the past and in this century, often in large quantities. In the 1960s it became increasingly obvious that certain chemicals had found their way into the natural environment in large quantities. Some of them came to be known as environmental poisons; animals exposed to them often displayed symptoms of illness or injury. Certain pollutants e.g. DDT, POPs, can, acting over long periods, harm living organisms even in low concentrations. This means that pollutants that are stable and thus persistent have a great ability to act as environmental poisons. Their stability means not only that their effects are long-lasting, but also that they are dispersed over large areas before being broken down [1]. There is a large growing public concern worldwide over these potential and actual deleterious effects on the environment and human health which calls for concern and search for solutions. Environmental analytical laboratories are important part of the solutions; as such quality environmental analytical instruments are needed in these laboratories. This research is focused on the state of the art of Nigeria' environmental analytical laboratories involved in environmental pollution control, many of these laboratories have been studied at different stage of this research, but only one will be reported here which is that of Kaduna Refining and Petrochemicals (KRPC) in Kaduna State of Nigeria.

For successful monitoring and policing of environmental pollution, excellent methods of assessment are needed. But there is confusion over the concept of methods for pollution studies, especially in oil spill often believed to be limited to the analysis of some specific polynuclear aromatic hydrocarbons by gas chromatography-mass spectroscopy. Analytical environmentalists believe that there is need for a hierarchical scheme of methods to be used in environmental assessment studies. Burns [2] illustrated the importance of using several complementary analytical methods in oil spill studies; she did this in tandem with examples from the results of the Buhia Las Minas oil spill study. In her work Burns went ahead to present further reasons why methods must continue to be developed for an expanded range of polar oxidation products. Whether new analytical methods as in Burns studies or old known ones, analytical methods can be divided into three as follows; separation technologies, molecular analysis and elemental analysis instrumentation. Common separation technologies instruments include Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC), Ion Chromatography (IC) and Electrophoresis. Molecular analysis instruments include Ultraviolet/Visible (UV/Vis) Spectrophotometer,

Infrared (IR) Spectrophotometer, Raman Spectrophotometer, Mass Spectrophotometer, Nuclear Magnetic Resonance (NMR), volta metric instrumentation and moisture analysis instrumentations [3]. For elemental analysis, instrumentations include Atomic Absorption Spectrometers (AAS), Atomic Emission Spectrometers (AES), X-ray instrumentation, surface analysis instrumentation, potential of hydrogen ions (pH) and ion-selective measurement instrumentation [3]. All these aspects are applied in environmental pollution monitoring in a standard environmental laboratory, therefore this research want to see how much of these are applied in the NNPC Kaduna laboratories and how their results from the available analytical instruments deal with pollution control.

Many researchers and manufacturers are dedicated to using and providing quality new and reliable instrumentation methods to ensure a healthy environment in our world. Of recent Jayaratne [4]. used fast-response monitors instrumentation, particularly they used TSI 3025A condensation particle counter (CPC) to measure particle numbers (PN) emitted by on-road vehicles. Another work on trying some new efficient methods was done by Jasdeep [5]. where they used immunochromatographic dipstick assay format using gold nanoparticles labelled protein-hapten conjugate for the detection of antrazine in water. This shows how much efforts the science world is putting into analytical methods in environmental pollution control. Another person's work on analytical instruments is that of Gillian [6], he showed that the analytical process is the science of taking measurements in an analytical and logical way to solve different problems such as in environmental pollution control. In matrix like environmental samples, identifying or quantifying an analyte in a complex sample becomes a serious excise in problem solving. To be efficient and effective, an analytical scientist must know the tools that are available to tackle variety of different problems. Gillian [6] describes these processes as shown in Figure 1 below where he showed that the analytical process is a logical sequence of steps that may take the form of a flow chat. In this chat Gillian place importance on all the steps including validation which many laboratories don't take serious.

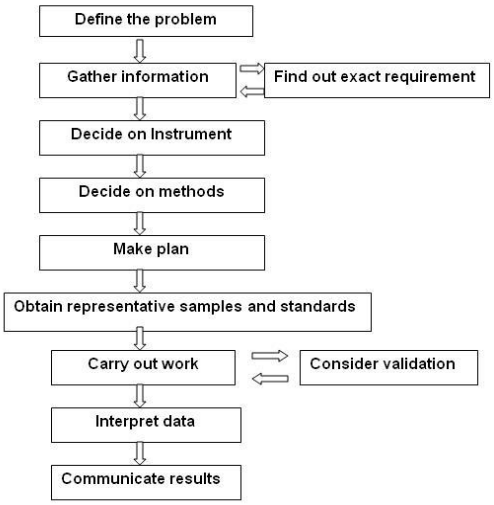


Figure 1 Analytical Process (Source; [6]

It can be seen that methods and analytical instruments cannot be taken lightly in environmental pollution control. Therefore this study is basically concerned with the analytical situations in environmental pollution control in the laboratory of Kaduna Refining and Petrochemicals Corporation (KRPC) Kaduna State of Nigeria. Some questions the study seeks to answer include how many of these analytical instruments discussed above are found in the NNPC Kaduna laboratory? How do the analytical results taken using available analytical instruments agree with the Nigerian Standard? etc

II. EXPERIMENTAL

The research was implemented in close collaboration with laboratory workers of Kaduna Refining and Petrochemicals Corporation (KRPC) Kaduna State of Nigeria.

As of the time of this research insitu measurements of waste water of the industry were done at four points as follows:

a) Before the waste water gets to the treatment tank
b) In the treatment tank (Figure1)
c) Before the treated water leaves to receiving river i.e. at the point where the treated water goes out
d) In the receiving river at the point of entrance (The receiving rivers are River Kaduna and Romi River).

In the insitu test very basic analytical instruments such as dissolved oxygen (DO) meter, PH meter incorporated with thermometer, conductivity meter and total dissolved solid meter were used.

Another set of results were taken from the NNPC Kaduna (KRPC) chemical laboratory. This

is because in this laboratory general control of the process, products and the environmental pollution are done. The chemical laboratory consists of water laboratory, oil laboratory and general laboratory. The water laboratory is where environmental pollution control is mostly carried out; they monitor the waste water, treated waste water and the receiving rivers. Results were taken here with instruments such as: PH meter, chemical oxygen demand (COD) meter/turbidity meter and double beam spectrometer. Water sample were collected in the morning from the three points and taken directly to the laboratory for immediate analysis using the above given analytical instruments. The insitu results were taken on different days as can be seen in the table, but the laboratory results were taken on one day.

III. RESULTS AND DISCUSSION

The results obtained from KRPC are shown below in Tables 1 to 3. The first two tables contain the insitu measurements results taken on different days and the third table contains the end of month chemical laboratory results, in which the production and waste water treatments are monitored.

Table 1 Insitu Results Obtained from NNPC (KRPC) Kaduna Environmental Pollution Control in 2007

Date Results Taken: 10:08 2007			
Points	PH	Conductivity	Temperature
A	7.48	28.7	29.4
B	7.51	32.5	30.2
C	7.40	31.2	30.1
D	7.17	34.5	27.8
Date Result Taken: 13:08 2007			
Points	PH	Conductivity	Temperature
A	7.36	16.80	27.9
B	7.37	16.84	27.6
C	7.26	19.10	28.1
D	6.76	31.70	29.7
Date Result Taken: 15.08. 2007			
Points	PH	Conductivity	Temperature
A	7.62	19.38	28.70
B	6.07	39.40	29.20
C	7.22	40.20	28.60
D	6.95	34.20	26.20
Date Results Taken: 16.08.2007			
Points	PH	Conductivity	Temperature
A	7.32	18.90	28.20
B	7.16	43.40	31.70
C	7.33	40.70	31.10
D	7.20	35.50	28.10

Table 2 Insitu Results Obtained from NNPC (KRPC) Kaduna Environmental Pollution Control in 2008

Date Results taken: 12:08 2008			
Points	PH	Conductivity	Temperature
A	8.13	1.00	29.10
B	7.97	0.76	38.40
C	7.72	1.22	35.90
D	7.28	2.00	33.30
Date Results Taken: 13.08.2008			
Points	PH	Conductivity	Temperature
A	8.10	0.80	27.20
B	7.80	0.60	36.20
C	7.62	1.10	35.70
D	7.16	1.72	33.00
Date Result taken: 14.08. 2008			
Points	PH	Conductivity	Temperature
A	10.96	1.80	31.60
B	10.88	1.26	35.50
C	11.08	1.36	34.50
D	7.82	1.82	34.40
Date Results Taken: 15.08.2008			
Points	PH	Conductivity	Temperature
A	7.64	1.21	30.30
B	7.65	0.86	36.6
C	7.44	1.20	34.70
D	-	-	-

Key
A = Waste water before its get to treatment tank
B = Waste water in treatment tank
C = Treated water before its leaves to receiving river
D = Treated water at the point of entrance into the receiving river

Table 3 NNPC Kaduna ChemicaLaboratory Month End Analysis Report- November 2008

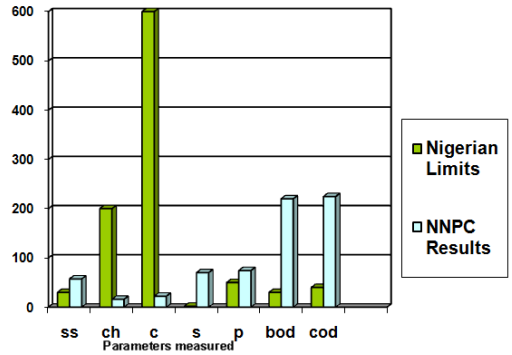
Parameters Analyzed	Kaduna River		Romi River			Refinery Effluent	
In ppm or mg/l except stated	Design Spec	Results	Design Spec	Up	Down	Design Spec	Results
PH	7.0-7.3	7.61	7-7.5	6.86	7.00	7-8.5	7.61
Conductivity (µs)	13-105	89.90	220-370	71.60	230.10		89.9
Total solids	38-3328	281.81	200-350	295.10	208.11		281.81
Suspended solids	18-3000	57.34	20-50	130.16	38.99	10.0mg/l	57.34
Turbidity (NTU)	20-3000	15.96	20-50	19.26	40.95	50.0	15.96
Alkanity M	20-62	44.00	62	40.00	42.00		44.00
Total Iron	0.02-5.5	ND	1.0	ND	ND	0.3mg/l	ND
Total Hardness	12-38	26.00	38	22.00	30.00	500 mg/l	26.00
Ca Hardness		16.00		16.00	20.00		16.00
Chloride	0.2-24.8	21.7	27.8	18.80	26.3		22.3
Silica (SiO2)	0.8-9.3	12.49	1.7				12.49
Sulphate		7.00	3.0	25.00	52.00	200mg/l	7.00
Phosphate		7.44		8.44	17.60		7.44
B.O.D.(5days)		92.80		76.50	103.40	25 mg/l	220.00
C.O.D		170.00	38.40	96.80	113.00	60.0 mg/l	170.00
Dissolved Oxygen		7.20		7.50	6.50	Nil	7.10
Total dissolve solids	70-326	224.47	350	164.94	169.22	2000 mg/l	224.47
Oil		ND		ND	ND	0.3 mg/l	ND
Hydrocarbons		ND		ND	ND	0.1 mg/l	ND
Phenols		ND		ND	ND		ND
Nitrate		0.30		0.04	1.00		0.30
Ammonia-N (mg/l)	1.0 as N	0.22		0.20	0.52	1.0	ND
Sulphide (H2S) (mg/l)	0.2	0.01		0.01	0.04	0.2	ND
Zinc (mg/l)	5.0	ND		ND	ND	5.0	ND
Lead (mg/l)	0.05	ND		ND	ND	0.05	ND
Arsenic (mg/l)		ND		ND	ND	0.05	ND
Cyanide (mg/l)	0.05	ND		ND	ND	0.05	ND
Cadmium (mg/l)		ND		ND	ND	0.05	ND
Boron (mg/l)		ND		ND	ND	0.05	ND
Selenium (mg/l)		ND		ND	ND	0.01	ND
Mercury (mg/l)		ND		ND	ND	0.000	ND
Temperature (oC)	36	28.8		25.6	28.1	36	28.3
Hexa Chromium	0.03	ND		ND	ND	0.03	ND

ND = Not Determined due to lack of equipments (instruments) and also faulty equipments (instruments)

Figure 1 below is a picture of the waste water treatment plant taken during this research. This is the point which the raw waste water entered from the plant, it can be seen in this picture how loaded the water is with waste like oil, grease, etc.

Figure 1 Waste Water Treatment Tank of NNPC Kaduna

To evaluate the NNPC waste water treatment, a comparison of their treated effluent values is done with the given limits in the Nigerian Guidelines and Standards for environmental pollution control [7, 8, and 9]. This comparison is shown in Figure 2 where the NNPC treated effluents values are shown in blue and the given limits in the Nigerian Guidelines and Standards for Environmental Pollution Control are shown in green.



SS= Suspended Solids, CH = Ca Hardness, C = Chlorides, S = Sulphate, P = Phosphate, bod =BOD, cod = COD

Figure 2 Comparison of Nigerian Effluents limits with NNPC Results

A critical component of environmental monitoring is the type of analytical instruments used to analyze samples. Normally the choice of these analytical instruments is dictated by the environment monitored, the parameters of interest and the data quality requirements. And one must select a scientifically sound method, approved by a regulatory agency, for example the Nigerian Federal Ministry for Environment.

The NNPC laboratory just use instruments that are available and not so much dictated by the regulatory agency nor the environment or parameters to be monitored as can be seen from what was obtained in the results. This is an unfortunate situation because analytical measurements are the foundation for determining pollutants and their effects in the environment and to ultimately formulate appropriate risk management policies and laws. Some of the pollutants enumerated in the result need very good analytical instruments to control them, because when dealing with certain types of pollutants like BTEX, dioxins, heavy metals, etc, the best means available need to be used to obtained accurate and reliable measurements. In NNPC chemical laboratory, the results given in Table 3 showed many test were not done because the needed instruments were not available or not in use. In front of many tests are given ND, i.e. "not determined" due to lack of equipment (instruments) and also faulty equipment. Pollutants like oil, hydrocarbons, phenols, zinc, lead, arsenic, cyanide, cadmium, mercury, etc cannot be determined in this laboratory for lack of instruments. That means in their day to day analysis the treated wastewater is discharged into the receiving river regardless of how much of these pollutants are found inside. Some of these pollutants not tested in NNPC Kaduna treated wastewater before its being discharged into River Romi are hazardous and should be determined to make sure it does not exceed allowed limits. In the Nigerian Guidelines and Standards for Environmental Pollution Control FEPA [10], some significant wastewater parameters for some selected industries are given. These parameters are mandatory to be tested to show that it has not exceeded allowed limits in the treated wastewater before discharging into the receiving water body. For the petroleum refining industries these parameters includes oil, phenol, lead, cyanide, chromium and zinc. Some of them have limits that are really very small such as lead has allowed maximum limit of 0.05mg/L. But for lack of instruments they are not even tested, which means a large amount could be going into the receiving river, which is a serious problem both to animals and plants.

In the comparison (Fig 2) above it can be seen that the value for Ca Hardness and Chlorides in the Nigerian limits are much higher which is good because that shows the NNPC results are below limits. But in the rest, in about 71% of the

results, the NNPC results are all well above the given limits, which is bad for the receiving river and the environment. Parameters like BOD and COD can drastically affect aquatic lives in the receiving river, since the loss of oxygen in the river can create stress on many aquatic organisms including fish. Therefore this result does not show good environmental pollution control for the company which will end up destroying the river and its aquatic inhabitants. In Table 4 one can see how many parameters have not been measured due to lack of analytical instruments or the instrument is faulty, this does not allow for efficient monitoring of the pollutants that may end up in the receiving river. This violate one of the principles of the Guidelines and Standards for Environmental Pollution Control in Nigeria which says, "It is mandatory for all industries to have industrial pollution monitoring capabilities within their own set up"[10]. For NNPC as one of the biggest oil producing company in the country to lack capability to measure parameters like oil in treated wastewater, phenols, etc is very damaging for the environment. These parameters that are not measured can be present in the effluent in a large quantity, which will go directly to the receiving river; this is unhealthy for humans, animals, plants and the environment at large.

Table 4 Comparison of Treated Effluent Values of NNPC Kaduna and Nigeria Effluent Limits

Parameters Analyzed (ppm or mg/l except stated)	Nigeria Limits	NNPC Results ND=Not Determined
PH	6.5 -8.5	7.61
Conductivity (µs)	-	89.9
Total solids	-	281.81
Suspended solids	30mg/l	57.34 mg/l
Turbidity (NTU)	-	15.96
Alkanity M	-	44.00
Total Iron	20mg/l	ND
Total Hardness	-	26.00
Ca Hardness	200mg/l	16.00 mg/l
Chloride	600mg/l	22.3 mg/l
Silica (SiO2)	-	12.49
Sulphate	0.2mg/l	7.00 mg/l
Phosphate	5mg/l	7.44 mg/l
B.O.D.(5days)	30mg/l	220.00 mg/l
C.O.D	40mg/l	170.0mg/l
Dissolved Oxygen	-	7.10
Total dissolve solids	2,000.mg/l	224.47 mg/l
Oil	10mg/l	ND
Hydrocarbons	5,000mg/l	ND
Phenols	0.5mg/l	ND
Nitrate	20mg/l	0.30
Ammonia-N (mg/l)	0.210mg/l	ND
Sulphide (H2S) (mg/l)	0.2mg/l	ND
Zinc (mg/l)	< 1mg/l	ND
Lead (mg/l)	0.05mg/l	ND
Arsenic (mg/l)	0.1mg/	ND
Cyanide (mg/l)	< 0.01	ND
Cadmium (mg/l)	< 0.01	ND
Boron (mg/l)	5mg/l	ND
Selenium (mg/l)	< 1mg/l	ND
Mercury (mg/l)	0.05mg/l	ND
PCBs	0.003	ND
Hexa Chromium mg/l	< 0.01	ND

IV. CONCLUSION

From the results and the analysis seen in Fig2 and Table 4, and from the literature [11 and 12] it can be concluded here that there are lack of good analytical instruments and so many parameters cannot be measured. From the results obtained and used to compare with the Nigerian standard in Table 4, some values are above the Nigeria standard, but the problem is that many parameters that can be of serious health effect to humans and aquatic leaves are not been measured. The conclusion here is that lack of needed analytical instruments in the chemical laboratory is a serious problem which needs to be addressed and solved for good environmental pollution control to be done in the chemical laboratory.

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