Determination of Heavy Metals Concentration in Wastewater of Warri Refinery and Petrochemicals Company (WRPC)

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ABSTRACT

Wastewater from some industries contains high levels of contaminant such as colloid, suspended, and dissolved minerals. Heavy metals have negative impact on all forms of life in the environment. Crude oil refining makes use of large volume of water, whence generate large quantities of wastewater which must comply with stringent environmental guidelines. To this end, several treatment methods have been explored to keep contaminants levels within limits. This study investigated the presence of heavy metals in discharged wastewater effluents from the premises of Warri Refining and Petrochemical Company LTD into the Ubeji creek. The analysis was carried out using the Flame Atomic Adsorption Spectrometry method. Standard solutions used for calibration were prepared for the five heavy metals analysed. Results showed average concentrations of chromium was….The results showed that effluent water from WRPC has concentrations of heavy metals within acceptable limits for discharge into the environment.

1.   INTRODUCTION

The oil or petroleum refinery is an industrial process plant where crude oil is refined into useful products such as naphtha, gasoline, diesel fuel, jet fuel, kerosene, fuel oil etc. Ethylene and propylene which are petrochemical feedstock can also be produced by direct cracking of crude oil. Every refinery has its specific design and layout for the production of desired products; hence no two refineries are the same (Gary and Handwerk, 2011).

Petroleum refining consist of different processes which begin with the fractional distillation of crude oils into separate hydrocarbon groups based on their boiling points (Kister, 1990). Most of the products are sometimes refined further into more economically viable products resulting sometimes in the change of their molecular structure through the processes of reforming, cracking, etc. A major aim of petroleum refining is to remove non-hydrocarbon impurities such as sulphure, oxygen and nitrogen compounds as well as heavy metals which adversely affect the quality of finished products (Chaudhuri, 2011). Chemical contaminants in petroleum include brines, arsenic, hydrocarbons, and heavy metals (nickel, vanadium, copper, cadmium, lead, chromium, zinc and selenium). Others include mercury, arsenic, tin, manganese, boron, iron and silver. The deleterious effect

of these contaminants on the environment and man is however mitigated by effective treatment to remove them before disposal. Petroleum refining requires large amounts of fresh water, consequently, large volumes of wastewater are generated and released into the environment. Wastewater from crude oil refineries is often characterized by toxic contaminants. Natural water bodies which receive these waste waters from refineries are polluted overtime, resulting in the reduction of dissolve oxygen with its concomitant adverse affect on aquatic life.

Different types of wastewater in petroleum refinery include Sour water (which is produced in the atmospheric and vacuum columns and is typically composed of ammonia and hydrogen sulphide), Cooling water from heat exchange units and Storm water/ Sewage water amongst others (Yokogowa, 2019).

Wokoma and Edori (2017) analysed the presence of heavy metals in an oily wastewater effluent. Their analyses showed that the concentration of heavy metals was in the order Zn > Fe > Pb > Cd. Also, Uzoekwe and Oghosaine (2011) investigated the effects of effluents released from a refinery on the environment. Results from the work showed that concentration of heavy metals ranged from 0 to 4.27 ppm and was in the order Fe > Cu > Zn > Cr > Ni >Pb> As >Vn> Cd and within prescribed limits of the Federal Ministry of Environment. Similarly, Israel, Obot et al. (2007) determined the presence of heavy metals in effluents of the Eleme Petrochemicals Company Ltd and also found that effluent discharged had metal concentrations within prescribed limits of the regulatory bodies. This present study is aim at determining the types of heavy metals in wastewater of the Warri Refining and Petrochemicals Company LTD and to examine the suitability or otherwise for the refinery wastewater to be discharged to the environment. Consequently, the study will help in keeping close and keen eye on activities of crude oil refineries vis-à-vis their environmental safety procedures. Thus, the study will help to create the much-needed database for reference purposes on effluents' metal content and provides good evidence of environmental compliance or not by the Warri Refining and Petrochemical Company LTD thereby reducing, if not eliminating disputes with host communities arising therefrom.

1.2   *Study Area*

The study area which is the Warri Refining and Petrochemical Company Ltd has coordinates of 5°34′05″ N, 5°43′00″ E, 33sq.m and is located in Ubeji, Warri, Delta State, Nigeria. WRPC was incorporated as a limited liability company on the 3rd of November, 1988. It was built for the sole purpose of efficient and profitable processing of crude oil into petroleum products, through efficient resource allocation, while exploiting new business opportunities (NNPC, 2017).

The landforms of Ubeji community consists of sedimentary basins and basement complex rocks (Ija et. al. 2003). This means that these rock formations allow for the permeability of fluids (Achudume, 2009). All effluents (treated or untreated) from the premises of WRPC are discharged into Ubeji creeks, which flows into the Ubeji river through the Crawford creeks and ends up in the Warri river. The major occupation of the people is fishing and depend on the creek as an outlet to the larger water (Uzoekwe and Oghosaine , 2011).

2.   MATERIALS AND METHOD

2.1   *Atomic   Absorption Spectrophotometer*

Atomic Absorption Spectrophotometer which operates on the principle of the Beer-Lambert's law (Tsade, 2016) was used for the analysis. The equipment atomizes sample by flame sources to form free atoms which absorb radiation at discrete wavelength that corresponds to specific elements. This analytical technique is simple to use. It analyzes different metals in a solution and has high sensitivity. Concentration is determined by this technique using the calibration curve and the equation of line as in the Beer Lambert's law:

$$A = \varepsilon LC$$

where;

$A = Absorbance$
$\varepsilon = Naperian\ extinction\ co-efficient$
$L = Path\ Length$
$C = Concentration$

Before use, the equipment was blanked with a 2% de-ionized water while standard solutions of the test metals were prepared for the analysis. The working standard of each metal to be analysed was read in the order of 0.25ppm, 0.50ppm, 0.75ppm, 1.0ppm respectively. Initial concentration
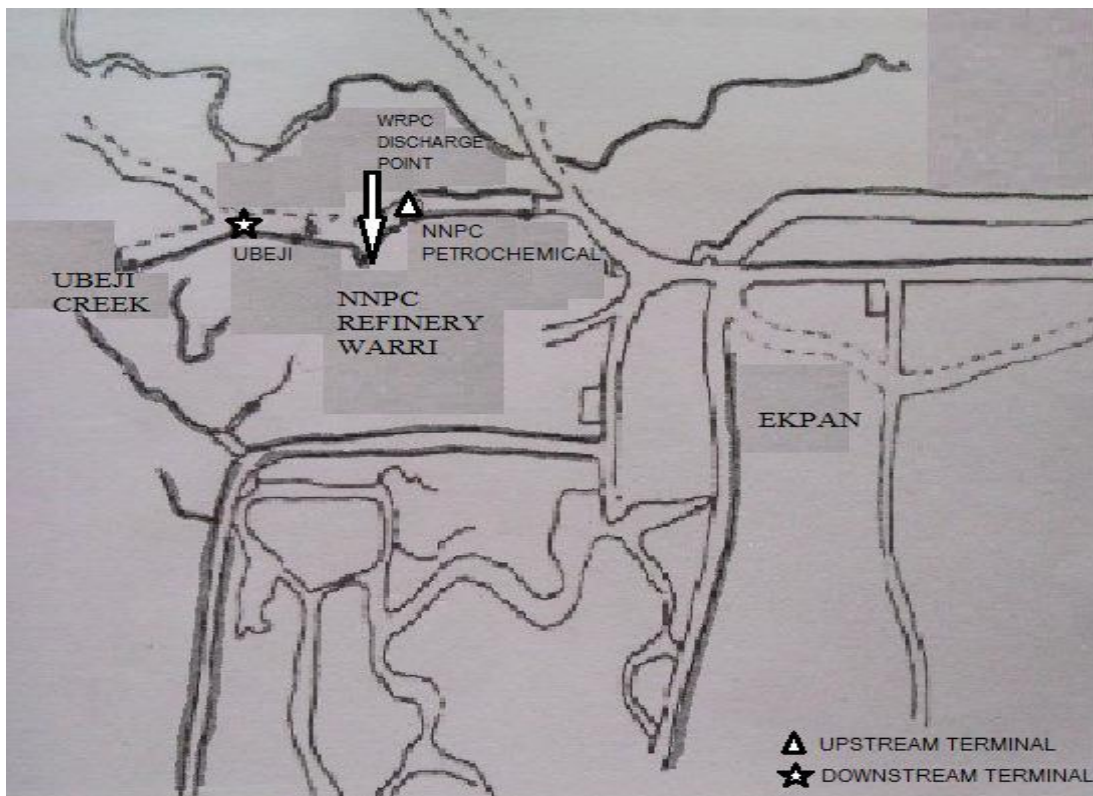

Fig 1: Study Area Map Showing WRPC

value (0.50ppm) was read after the sample (wastewater effluents) had been analysed. The continuous calibration value (0.50ppm) was read finally. This procedure was carried out for all heavy metals.

2.2 *Sampling Method*

Wastewater samples were collected with 50cl plastic cans at two different points; at the final effluent discharge point (Outflow channel) where treatment has taken place and the train channel which holds effluents yet to be treated. Before sample collection, the plastic cans were rinsed with hydrochloric acid to decontaminate them and dechlorinized by rinsing with water. The wastewater samples were taken to Analtrace Environmental Consultants and Laboratories Ltd. for heavy metal analysis.

2.3 **Sample Digestion Procedure**

100ml of the sample was measured and poured into the beaker. Using the dropper, 4ml of 1:1 HNO_3 solution was added to the sample and heated (refluxed). Refluxing continued for about 45 minutes to one hour until about 20ml of the solution remained. The beaker is covered with a watch glass during heating to prevent evaporation. a colour change of the solution from light

yellow to clear indicates completion of digestion. Once, the heating process is complete, the remaining solution is filtered into a 100ml volumetric flask. Distilled water is then used to make-up to the meniscus mark. This procedure is repeated for every other metal digested.

3. **RESULTS AND DISCUSSION**

Results of heavy metals analysis from wastewater of the Warri Refining and Petrochemical Company Ltd are given in Table 1 and Table 2.

Concentration of chromium ranged from < 0.05ppm in the Outfold Channels to 1.0ppm in Train Channel B. This result is consistent with the fact that waters in the Outfold Channels have been treated for contaminant reduction and/or removal (WRPC, 1978), which is not the case with that from the train channel. However, noteworthy is the significant difference in concentration between samples from Train Channel B and Train Channels A and C (see calibration graph of Figure 2). This may be resultant from the source of such wastewater in the plant.

Table 1: Heavy Metals Analysis from Wastewater of the Warri Refining and Petrochemical Company Ltd

S/N	Sample ID	Parameters					Method
	(ppm)	Chromium	Iron	Zinc	Manganese	cadmium	
1	Out fold CH. A	< 0.05	2.392	1.169	0.121	< 0.001	FAAS
2	Out fold CH. B	< 0.05	2.400	1.162	0.159	< 0.001	FAAS
3	Train CH. A	0.05	2.575	1.332	0.114	< 0.001	FAAS
4	Train CH. B	0.1	2.650	1.307	0.159	< 0.001	FAAS
5	Train CH. C	0.05	2.358	1.335	0.174	< 0.001	FAAS

TABLE 2: Table Showing Average Values of Concentration

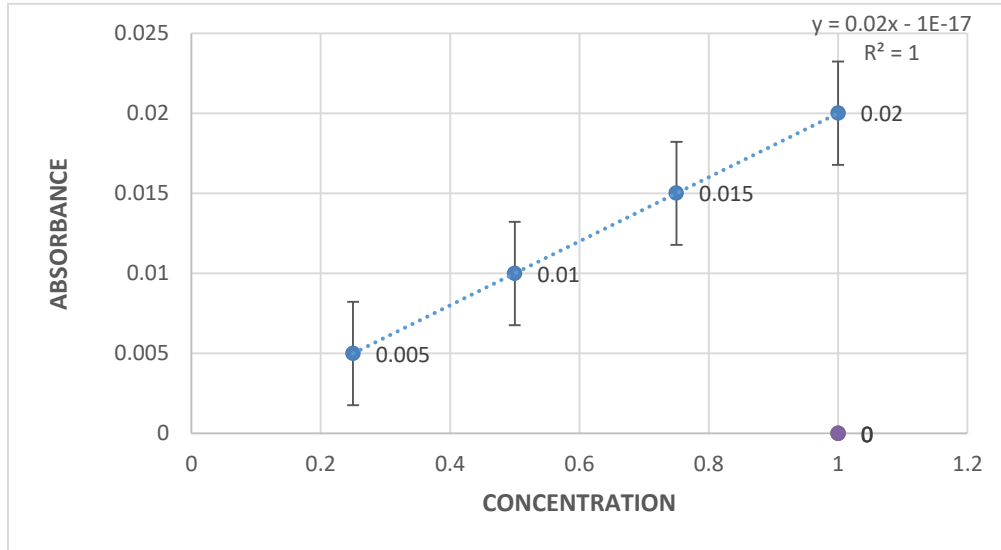| Sample I.D (ppm)	Chromium	Iron	Zinc	Manganese	Cadmium
Out fold Channel	< 0.05	2.396	1.166	0.140	< 0.001
Train Channel	0.06	2.535	1.133	0.149	< 0.001

Fig 2: Calibration Curve for Chromium

The concentration profile for iron is similar to that of chromium even though it showed markedly higher average values of 2.40 and 2.54 for Outfold and Train Channels respectively. Train Channel B also recorded the highest concentration of 2.65ppm while Train Channel C the lowest value of 2.39ppm (See Figure 3). This discrepancy in concentration of iron between the out fold and Train Channels may be the result of difference in corrosion of the local pipes conveying the fluids. The concentrations of Iron detected in the wastewater effluents were lower than the standard of USEPA but were higher than the standard limits of the Federal Ministry of Environment.
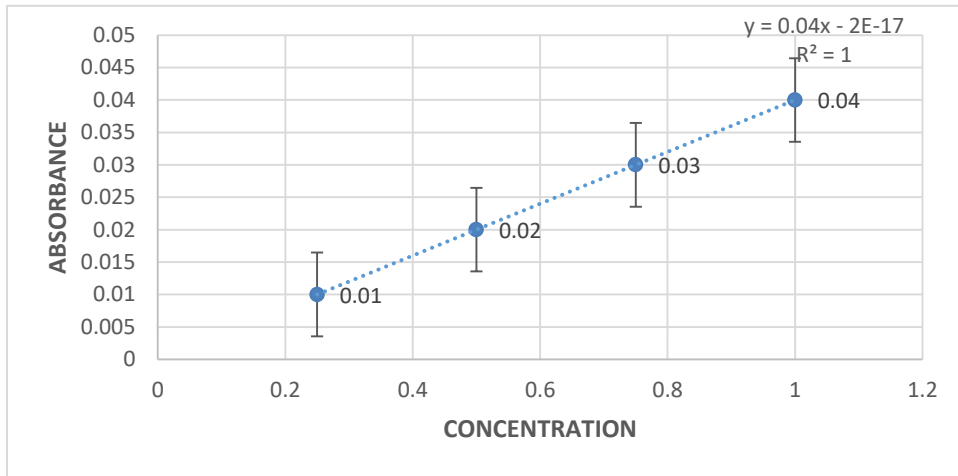
Fig 3: Calibration Curve of Iron

Zinc concentrations averaged 1.16 and 1.33 for the outfold and Train Channels respectively, but rather surprisingly Train Channel sample C had the lowest concentration of 1.307 in the Train Channels as against the previous samples (see Table 1 and Figure 4). The Zinc concentrations are well below the Federal Ministry of Environment of Nigeria standard of 3.0ppm but slightly above the World Health Organization (WHO) recommendation of 1.0ppm.
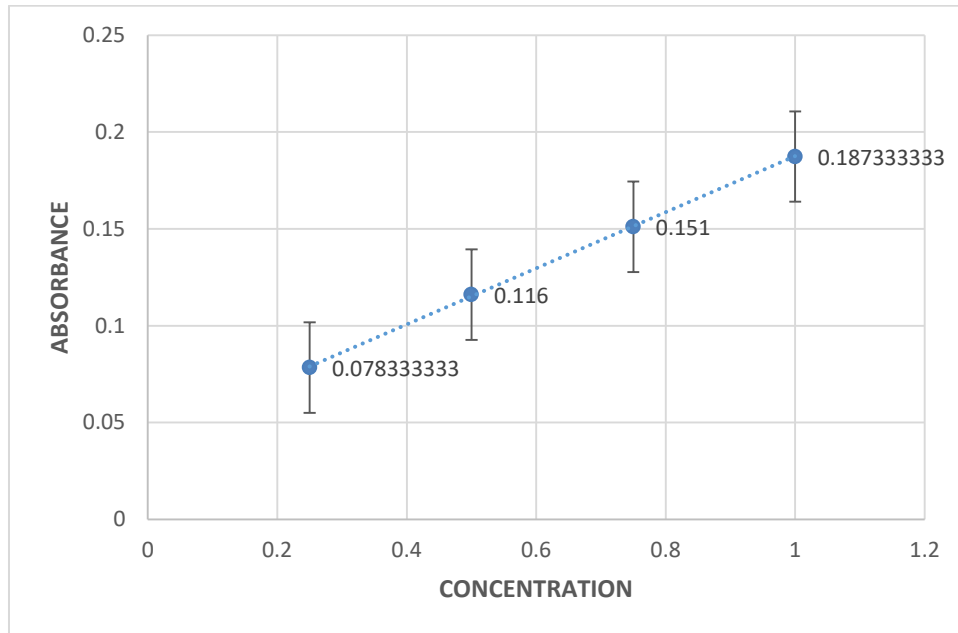

Fig 4: Calibration Curve for Zinc

Similar concentration profiles were recorded for manganese with average values of 0.140 and 0.149 for the outfold and Train Channels respectively (see Table 2 and Figure 5) while cadmium had the same concentration of < 0.001ppm for all Channel samples (Table 2 and Figure 6). The implication is that cadmium concentrations

are quite minimal that is not affected by the effluent treatment processes of the plant.
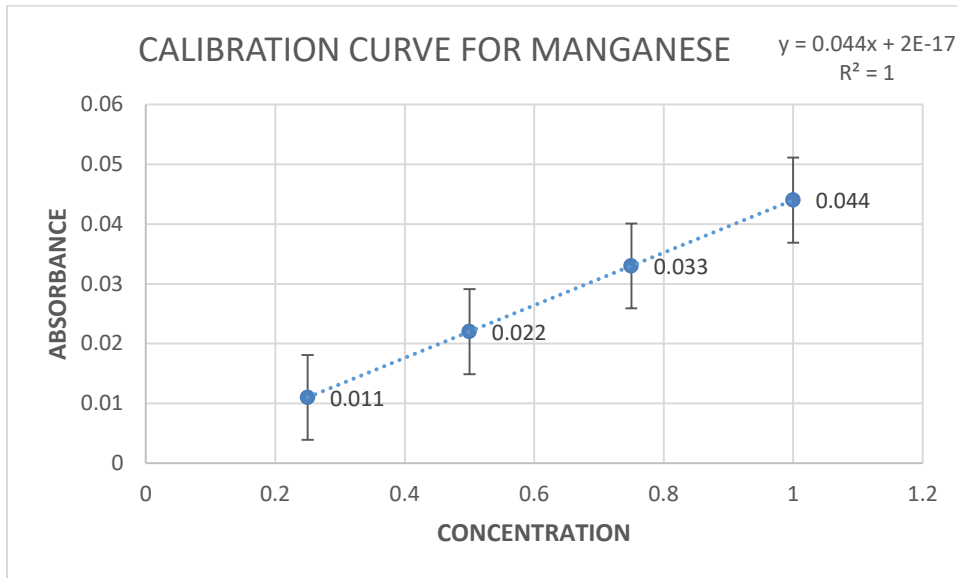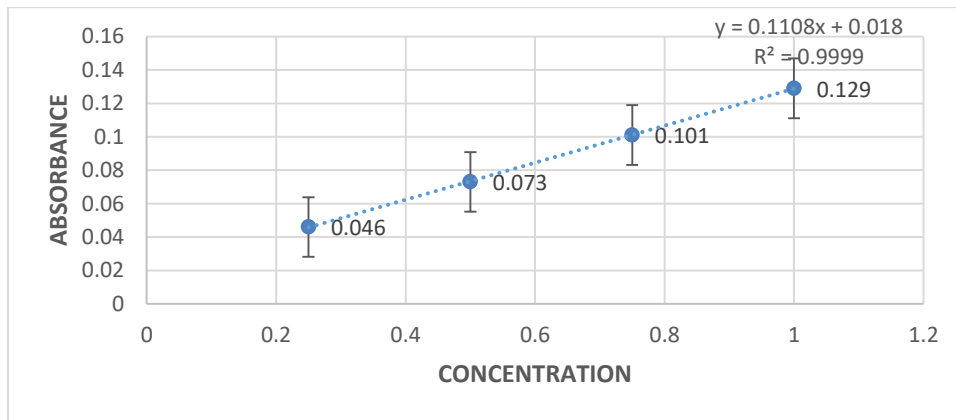

Fig 5: Calibration curve for Manganese

Fig 6. Calibration Curve for Cadmium

TABLE 3: Standard guidelines by Regulatory Agencies

Metal	WHO 2018 (mg/L)	USEPA (mg/L)	FM Env (mg/L)
Chromium	N/A	0.1	0.05
Iron	3.0	N/A	0.30
Zinc	1.0	N/A	3.0
Manganese	N/A	N/A	0.2
Cadmium	0.02	0.005	0.003

4. CONCLUSION

The work showed that Iron, Zinc, and Magnesium concentrations were significantly higher than those of Chromium and cadmium which had extremely low concentrations in the wastewater. Also, all metals analyse had concentrations within permissible limits by the Federal Ministry of Environment of Nigeria, except concentrations of Iron. The forgoing requires that the WRPC may improve its wastewater treatment process to further reduce the concentration of iron in it or inspect its flowlines for change of possibly corroded ones.

Similarly, the concentration of Zinc is above the recommendation by the World Health Organization but well below the standard of the Federal Ministry of Environment of Nigeria. Since the later is the primary regulatory body in Nigeria, this concentration levels of Zinc can be sustained. Finally, the study revealed heavy metals concentration of effluents in the order: $Fe > Zn > Mn > Cr > Cd$. This result is consistent with the work of Uzoekwe and Oghosaine (2011) but slightly different from that of Wokoma and Edori (2017) which recorded higher concentrations of Zinc than Iron.

References

Abhishek, T.S., Sunil, (Dr.) J. K. and Meera, T.S. (2017). Oil Industry-Analysis, Effects and Removal of Heavy Metals. International Journal of Engineering, Sciences and Research Technology. 6(10): 254-255.

Achudume, A. C., (2009). The Effect of Petrochemical Effluent on the Water Quality of Ubeji Creek in Niger Delta Region. Bull Environmental Toxicology. 83: 410-415.

Bashorun, J.O and Olamiju, I.O (2013). Environmental Pollution and Refinery Operations in an Oil Producing Region of Nigeria: A Focus on Warri Petrochemical Company. IOSR Journal of Environmental Science, Technology and Food Technology. 2(6):18-23.

Chaudhuri, U. R. (2011), Fundamentals of Petroleum and Petrochemical Engineering, CRC Press, Boca Baton, pp.9

Gary, J.H and Handwerk, G.E. 2001. Petroleum refining: Technology and economics, 4th ed. Marcel Dekker, Inc.

Israel, A.U. Obot, I. B., Umoren, S. A., Mkpenie, V. and Ebong, G.A., (2007). Effluents and Solid Waste Analysis in a Petrochemical Company- A Case Study of Eleme Petrochemical Company LTD, Port-Harcourt, Nigeria. E-Journal of Chemistry. 5(1): 74- 79.

Kister, H. Z. (1990), *Distillation Operations*, McGraw Hill, New York

Mohamed, E., Saliema, A. G.Ali, M., Nawal, M.S. (2015). Determination of Some Heavy Metals in Raw Petroleum Wastewater Samples Before and After Passing on Australis Phragmites Plant. American Journal of Environmental Protection.4 (6): 354-356.

www.nnpcgroup.com, retrieved on September 30, 2017.

Oguzie, F. A. and Okhagbuzo, G. A. (2010). Concentrations of Heavy Metals in Effluents Discharges Downstream of Ikpoba River in Benin City, Nigeria. African Journal of Biotechnology.9(3):319-325.

Smith, R.A.(2010). Laboratory Manual for the Determination of Metals in Water and Wastewater by Atomic Adsorption Spectrophotometry. Graphic Art Division of the CSIR, Pretoria, South-Africa. pp 1-25.

Tsade, H.K. (2016). Atomic Absorption Spectroscopic Determination of Heavy Metals Concentrations in Kuluto River, Arbaminch, GamoGafo, Ethiopia. Journal of Environmental Analytical Chemistry. 3(1): 1-3.

Uzoekwe, S.A and Oghosanine, T.A., (2011). The Effect of Refinery and Petrochemical Effluent on Water Quality of Ubeji Creek, Warri, Southern Nigeria. Ethiopian Journal of Environmental Studies and Management. 4:107-112.

Wokoma, O.A.F and Edori, O.S., (2017). Heavy Metals Content of an Oily Wastewater Effluents from an Oil Firm at the Point of Discharge. Interpretation Journal of Chemistry, Pharmacy and Technology. 2 (4):154-161.