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# Determination of heavy metals concentration in waste water of Warri Refining and Petrochemicals Company (WRPC)

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## Abstract

Waste water from some industries contain 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 waste water which must comply with stringent environmental guidelines. To this end, several treatment methods have been explored in order to keep contaminants levels within limits. This study investigated the presence of heavy metals in discharged waste water 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 solution used for calibration were prepared for the five heavy metals analysed. Results showed average concentrations of chromium was within the acceptable limit. The overall results show that effluent water from WRPC has concentrations of heavy metals that is within the prescribed acceptable limits for discharge into the environment.

**Keywords:** Heavy metals, refinery, waste water.

## 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 & 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 sulphur, 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 & 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 waste water are generated and released into the environment. Waste water from crude oil refineries are often characterized by toxic contaminants. Natural water bodies which receives 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 waste water 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 waste water 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 found that effluent discharged had heavy metal concentrations within prescribed limits of the regulatory bodies.

Heavy metal contamination of water bodies and soil has been a problem with mankind for a long time. While they exist naturally in soil and rock formations, there is aggravated environmental impact of these substances from industrial activities. Crude oil refining is one industrial process that produces effluents with heavy metals, hence the study to ascertain their presence and concentrations in refinery waste water. The environmental and health implications of heavy metal contamination cannot be overemphasized (Bashorun & Olamiju, 2013). Consequently, the study will help in keeping close and keen eye on activities of crude oil refineries vis-à-vis their environmental safety procedures. Also, the study will help create the much needed database for reference purposes on effluents' metal content. Finally, the work provides good evidence of environmental compliance or not by the Warri Refining and Petrochemical Company LTD thereby reducing, if not completely eliminating disputes with host communities arising therefrom. This research work is therefore aimed at determining the types of heavy metals and their concentration found in the waste water of the Warri Refining and Petrochemicals Company LTD. It is also aimed at examined the suitability or otherwise of the waste water from the refinery for discharge into our environment.

### 1.1 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 & 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 & Oghosaine , 2011).

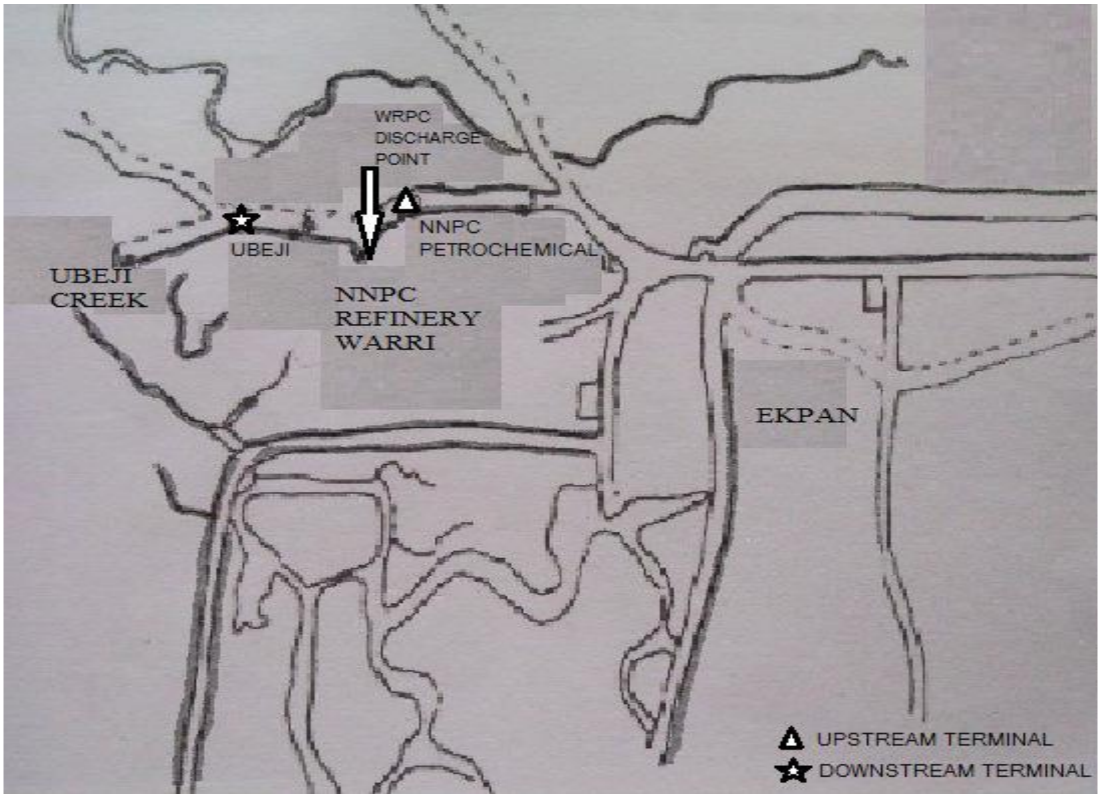


**Figure 1.1: Study area map showing WRPC**

## 2.Materials and method

### 2.1Atomic 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:

$$A = \varepsilon LC \quad (1)$$

where;
$A = \text{Absorbance}$ $\varepsilon = Naperian\ extinction\ co-efficient,$ $L = Path\ Length$ and $C = Concentration$

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 value (0.50ppm) was read after the sample (waste water effluents) had been analysed.

The continuous calibration value (0.50ppm) was read finally. This procedure was carried out for all heavy metals.

**2.2Sampling method**

Waste water 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 waste water samples were taken to Analtrace Environmental Consultants and Laboratories Ltd. for heavy metal analysis.

**2.3Sample 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 waste water of the Warri Refining and Petrochemical Company Ltd are given in Table 1 and Table 2.

**TABLE 1: Results of measure heavy metals parameters**

| S/N | Sample Id (ppm) | Parameters Chromium | Iron | Zinc | Manganese | cadmium | Method |
|---|---|---|---|---|---|---|---|
| 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 |

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 (calibration graph of Figure 1). This may be resultant from the source of such waste water in the plant.

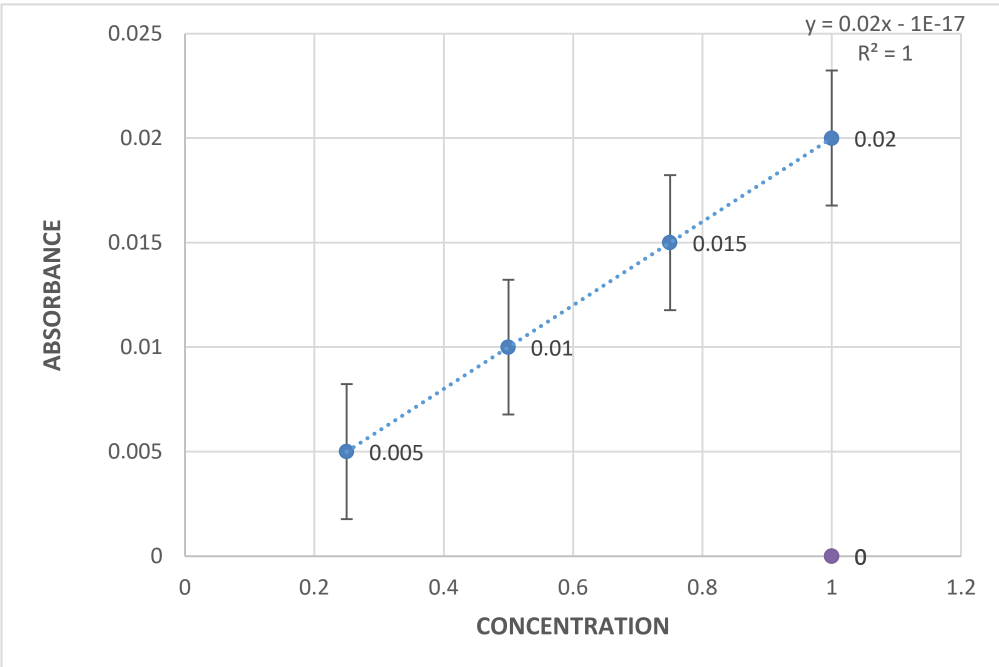


**Figure 1: Calibration curve for chromium**

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 as shown in Figure 2. 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 waste water effluents were lower than the standard of USEPA, but were higher than the standard limits of the Federal Ministry of Environment.

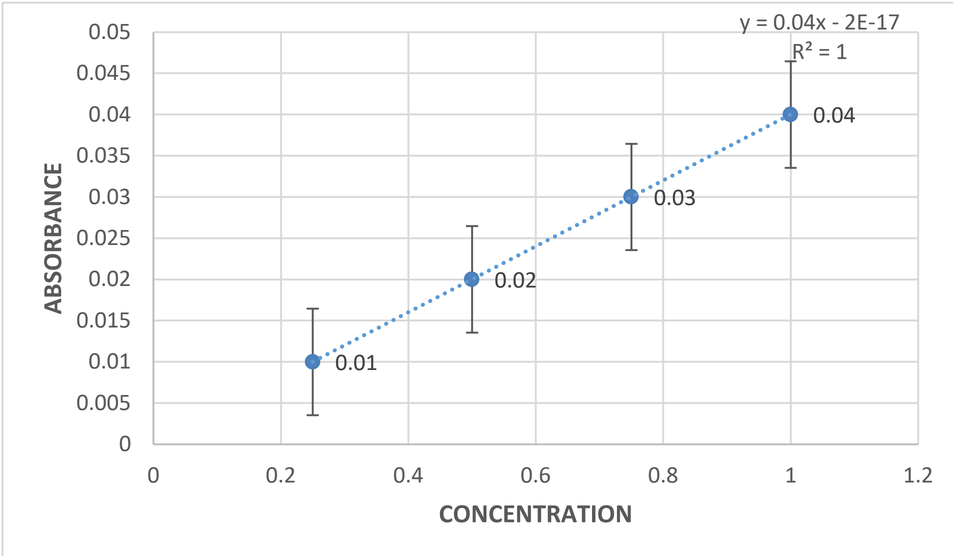


**Fig 2: Calibration curve of iron**

Zinc concentrations averaged 1.16 and 1.33 for the out fold 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 3). 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.

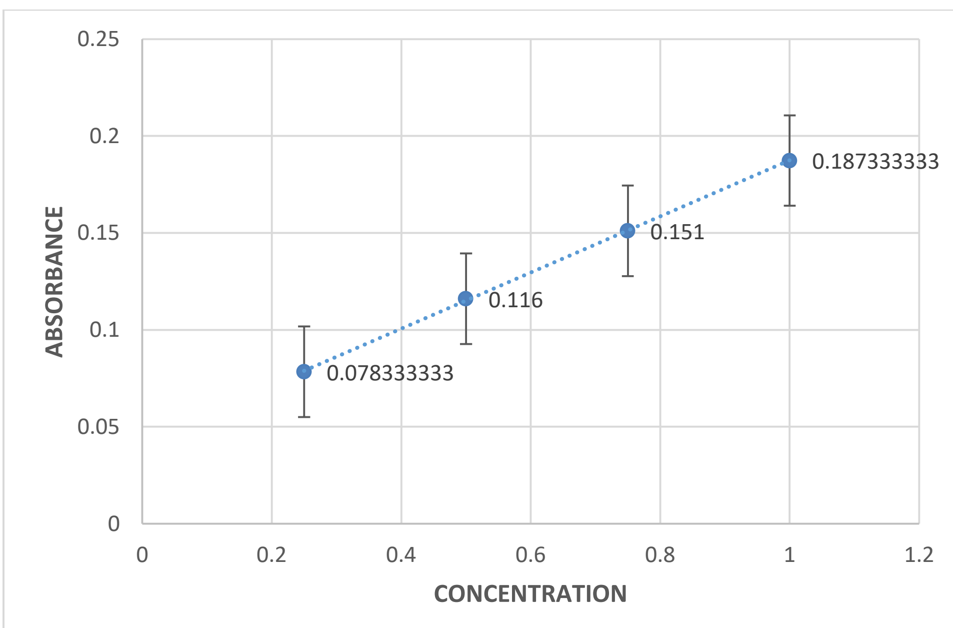


**Fig 3: Calibration curve for zinc**

Similar concentration profiles were recorded for manganese with average values of 0.140 and 0.149 for the out fold and Train Channels respectively (see Table 2 and Figure 4) while cadmium had the same concentration of < 0.001ppm for all Channel samples (Table 2 and Figure 5). The implication is that cadmium concentrations are quite minimal that is not affected by the effluent treatment processes of the plant.

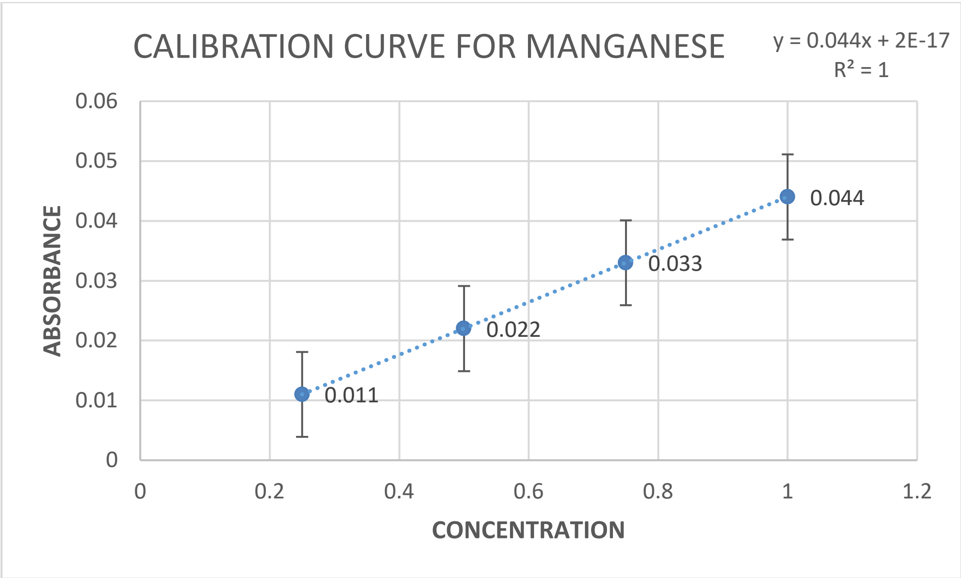


**Fig 4: Calibration curve for manganese**

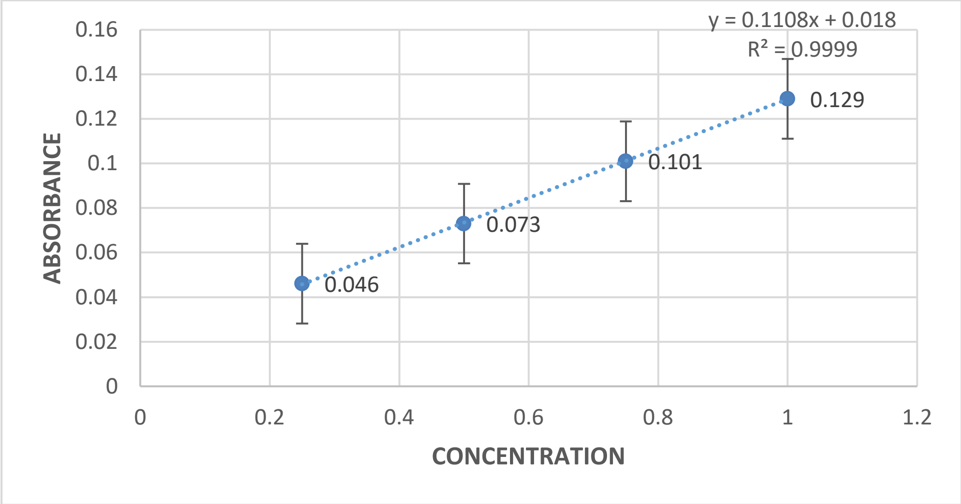


**Fig 5: Calibration curve for cadmium**

**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 |

*Source: Federal Ministry of Environment, 2016 Bulletin*

## 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 waste water. Also, all metals analyzes 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 waste water 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.

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