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*Full Length Research Paper*

# Concentration of benzene and phenol in some petroleum based industrial effluents in kaduna metropolis, Nigeria.

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**Concentrations of benzene and phenol were determined in effluents from four petroleum based industries coded as KP, TL,OL(I) and OL(II), using GC/mass spectrometer. The average concentrations of benzene in effluent samples of KP, TL and OL(II) were 0.48ppm, 0.59ppm and 0.50ppm respectively, and that of phenol in OL(I) and TL were 3.84ppm and 4.13ppm respectively. The values obtained were found to be higher than EPA standard limits.**

**Keywords:** effluents, carcinogenic, gas chromatography/mass spec., pollution, environment, benzene, phenol.

## INTRODUCTION

Petroleum industries generate wastes, some of which may be considered hazardous because of the presence of toxic organics and heavy metals (Obot *et at*., 2008). Accidental discharges as a result of abnormal operations, especially from the refineries and petrochemical complexes and lubricant blending plants, can be a major environmental hazard, releasing large quantities of pollutants into the environment (Beg *et al*, 2001).

Different kind of pollutants affect human beings unknowingly because the chronic effects are not dramatic compared to the acute menace (Nubi and Ajuonu, 2011). Pollution of soil, ground water and surface water often occurs as a result of spills and leakages of pollutants, as well as regular discharge from processing activities (NORAD, 1996), thus creating the potential for considerable health risks for the populace.

Nubi and Ajuonu, (2011) had reported that surface and ground water sources in Nigeria have been grossly contaminated by biodegradable organic compounds, toxic and hazardous substances including metals and pesticides, and therefore are not clean.

Wastewaters released by petroleum industries are characterized by the presence of large quantities of polycyclic and aromatic hydrocarbons, phenols, metal derivatives, surface-active substances, sulphides, naphthalenic acids and other chemicals (Obot *et al*, 2008). Due to the ineffectiveness of water treatment systems in many industries, their effluents may become seriously dangerous, leading to the accumulation of toxic products in the receiving water bodies with potentially serious consequences on the ecosystem (Bay *et al*., 2003).

Several investigations have shown positive correlation between petroleum industrial pollutions and the health of aquatic organisms. Another observation suggested a

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correlation between contamination of water and sediments with aromatic hydrocarbons from petroleum effluent and compromised fish health (Kuehn *et al*., 1995). The compositions of effluents from petroleum industries are regulated by various laws, however, it is not known whether they comply with the legally accepted toxicant levels for petroleum industries in Nigeria (Otokunefor and Obiukwu, 2005).

Petroleum has played an important role in the economy of some petroleum producing countries, but the ecosystem close to petroleum industries has been subjected to destruction by petroleum product spillage and other forms of pollutants discharges resulting from operational activities (Adeniyi and Afolabi, 2002). The compositions of the effluents have serious toxicological effects on aquatic environment and humans. The oil content of refinery effluents causes among other things depletion of dissolved oxygen (DO), loss of biodiversity and eutrophication in the receiving water bodies (Uzoekwe and Oghosanine, 2011). Crude oil, refined petroleum products, as well as polycyclic aromatic hydrocarbons are ubiquitous in various environmental compartments. They can bioaccumulate in food chains where they disrupt biochemical or physiological activities of many organisms, thus causing carcinogenesis of some organs, mutagenesis in the genetic material, impairment in reproductive capacity and / or causing hemorrhage in exposed population. The cause / effect of oil pollutant are usually quantified by using biological end point parameters referred to as biomarkers. Contamination of soil arising from spills is one of the most limiting factors to soil fertility and hence crop productivity (Onwura *et al*., 2007). Short term toxicity in fishes includes lymphocytosis, epidermal hyperplasia, hemorrhagic septicaemia (Beeby, 1993).

Majority of processing plants for oil and gas production consist of closed systems. This means that it will be very easy to monitor the kinds of waste being produced that require further treatment. However, some developing countries lack adequate waste management systems. This may be particularly problematic with regards to hazardous waste, such as oil-containing waste, heavy metals etc (NORAD, 1996). The effluent treatment plant available in OL and TL plants is the oil – water separator pits, which separates oil from water by gravity. The separated oil on top of water is then skimmed off. At this time, concentration of oil and grease, and other parameters being monitored in monthly effluent analysis, are expected to have reduced. And the wastewater is then discharge into the environment. However, it has been established that some soluble, carcinogenic organic compounds are not easily removed from the effluents by this treatment process (Utvik, 2003)

This paper assessed the presence of benzene and phenol in the effluents discharged into the environment from four selected petroleum industries within Kaduna metropolis of Nigeria code OL(I), OL(II), TL and KP. In addition, the concentration of these pollutants were compared with united state environmental protection agency (EPA) maximum permissible limits and the implications to public health were discussed.

The international agency for research on cancer (IARC) classified benzene and phenol in group 1 and 3 respectively (IARC, 2011). The national toxicology program (NTP) and the national pollution inventory (NPI) also identified benzene as a known human carcinogen (NTP, 2011; NPI, 2009).

## MATERIALS AND METHODS

Reagents used in this work were of analytical grade and were used without further purification. These include: sodium hydroxide (NaOH) 10 mol/dm$^3$, sulfuric acid ($H_2SO_4$) 50 %, methylene chloride ($CH_2CL_2$) (ACS 99.5 %) and distilled water.

Glasswares and equipment: Separatory funnel – 2000 cm$^3$, erlenmeyer flask – 250 cm$^3$, beaker – 100 cm$^3$, measuring cylinder – 100 cm$^3$, reagent bottles – 250 cm$^3$, and sample bottles – 250 cm$^3$ ; 2500 cm$^3$– amber glass bottles, retort stand assembly, oven, GC/MS system – QP2010 PLUS SHIMADZU, desicator, refrigerator and pH paper.

The research was carried out between April to August 2012, in Nigerian Defence Academy Kaduna, Nigeria.

### Sample Collection, Preservation and Handling

Samples were collected from effluent channels from KP, OL(I), OL(II) and TL. 1000 cm$^3$ of the wastewater was sampled from each sampling station (using glass sampling bottle) in the morning, afternoon and evening. The sampling processes were conducted for three days within the week and a total of nine samples were obtained.

The stated sampling procedure was applied in all the sampling stations.

All samples were refrigerated at 4°C from the time of collection until extraction.

All samples were extracted within seven days of collection and completely analyzed within 40 days of extraction.

### Extraction

1000cm$^3$ of the sample was transferred quantitatively into a cleaned and dried separatory funnel. The pH of the sample was adjusted to more than 11 with 10 mol/dm$^3$ sodium hydroxide solution. Methylene chloride (60 cm$^3$) was added to the pH adjusted content in the separatory funnel and extracted by shaking the funnel for two minutes with

**Table 1.** Average concentrations of benzene and phenol at various sampling sites.

| Sampling stations | Concentration of benzene (ppm) | | | | Concentration of phenol (ppm) | | | |
|---|---|---|---|---|---|---|---|---|
| | morning | afternoon | evening | average | morning | afternoon | evening | average |
| OL(I) | ND | ND | ND | ND | ND | ND | 3.84 | 3.84 |
| OL(II) | 0.16 | 0.58 | 0.77 | 0.50 | ND | ND | ND | ND |
| TL | ND | 0.59 | ND | 0.59 | ND | ND | 4.13 | 4.13 |
| KP | 0.79 | 0.16 | ND | 0.48 | ND | ND | ND | ND |
| **EPA limit** | | | | 0.2 | | | | 0.2 |

periodic venting to release excess pressure. The methylene chloride layer was allowed to separate from the aqueous phase for a minimum of 10 minutes. The methylene chloride extract was collected in a 250 $cm^3$ erlenmeyer flask. This extraction procedure was repeated two more times and all the methylene chloride extracts were put together and labeled as base fraction. The pH of the aqueous phase was then adjusted to less than 2 by adding sulfuric acid (50% solution) drop-wise. The acidified aqueous phase was extracted three times with 60 $cm^3$ aliquots of methylene chloride. All the extracts were put together and labeled as acid fraction. The base and acid fractions obtained above were kept for GC-MS analysis.

The above procedure was repeated for all the samples which were prepared and kept for GC-MS analysis.

## RESULTS AND DISCUSSION

The average concentrations of benzene and phenol detected in the samples were reported as in Table 1.

From Table 1, benzene was not detected in the morning, afternoon and evening effluent samples collected from OL (I). Phenol was not detected in the morning and afternoon samples but was detected in the base extract of the evening samples with concentration 3.84 ppm.

In the effluent samples from OL (II), benzene was detected in the base extract of the morning samples (0.16 ppm), afternoon samples (0.58 ppm) and evening samples (0.77 ppm). Phenol was not detected in any of the samples.

In the samples collected from TL, benzene was not detected in the morning and evening samples but was detected in the base and acid extracts of the afternoon samples with concentration 0.59 ppm. Phenol was not detected in the morning and afternoon samples but was detected in the base extract of the evening samples with concentration 4.13 ppm.

In the samples collected from KP, benzene was detected in the acid extracts of the morning sample (0.79 ppm) and the afternoon samples (0.16 ppm) but was not detected in the evening samples. Phenol was not detected in all the samples.

The average concentration of benzene in OL (II) (0.50 ppm), TL (0.59 ppm) and KP (0.48 ppm) were higher than the permissible limit (0.2 ppm) and the maximum contaminant level (MCL) for benzene in drinking water which is 0.05ppm, (USATSDR, 2010).

The average concentration for phenol in OL (I) (3.84 ppm) and TL (4.13 ppm) were higher than the permissible limits 0.2ppm, (Alejandro *et al*, 2010).

High concentration of benzene increases the risk of cancer and other illnesses in human and other animal.

The presence of benzene and phenol in the effluents of these industries may partly be due to the stains of base oils, additives, engine oil, premium motor spirit (PMS), automotive gas oil (AGO), low pour fuel oil (LPFO) on the floor of these industries, in which degreasers are used to wash. These oils are hydrocarbon based and therefore may be responsible for the presence of the carcinogenic organic compounds detected in the wastewater.

Michel (1992) had documented that carcinogenic organic compounds of crude oil hydrocarbons range include small-ringed benzene, toluene, xylene, kerosene gasoline and naphthalene. It does appear that the carcinogenic organic compounds obtained in this work compare favourably.

## CONCLUSION

It can be concluded that benzene and phenol are present at concentrations higher than EPA acceptable limits in the effluents of these industries. Therefore there is need for improvement in the effluent treatment process in these industries so as to reduce the pollution load which has serious consequences on the aquatic environment.

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