Original Research Paper

Concentration of Oxirane and Naphthalene in Selected Petroleum Based Industrial Effluents in Kaduna Metropolis, Nigeria

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ABSTRACT

Concentrations of oxirane and naphthalene were determined using GC/Mass spectrometer (model- QP201 Plus Shimadzu), in effluent samples from four selected petroleum based industries in Kaduna metropolis, Nigeria, coded as KP, TL, OL(I) and OL(II). Oxirane was detected in the morning, afternoon and evening samples of OL(II), morning and afternoon samples of KP and afternoon samples of TL. While naphthalene was detected in afternoon samples of OL(I) and evening samples of KP. The average daily concentrations of oxirane and naphthalene were: oxirane {KP(12.1 ppm); TL(15.05 ppm); and OLII (11.25 ppm)} and naphthalene {OLI (0.47 ppm); KP (0.51 ppm)}. The results were compared with EPA standard limits. Naphthalene concentrations were within the acceptable limits while oxirane concentrations were higher than the limits.

INTRODUCTION

One of the most critical problems of developing countries such as Nigeria is improper management of wastes generated by various anthropogenic activities (Kanu and Achi, 2011). More challenging is the unsafe disposal of these wastes into the ambient environment. Water bodies especially freshwater reservoirs are the most affected (Kanu and Achi, 2011). This is because most industries in Nigeria discharge their effluents into freshwater bodies (rivers, streams etc). The improper disposal of wastes have often rendered the natural resources unsuitable for both primary and secondary usage. Industrial effluent contamination of natural water bodies has emerged as a major challenge in developing and densely populated countries like Nigeria (Kanu and Achi, 2011). Petroleum has played an important role in the economy of some petroleum producing countries, but the ecosystem close to petroleum industries have been subjected to destruction by petroleum product spillage and other forms of pollutants discharges resulting from operational activities (Adeniyi and Afolabi, 2002).

Petroleum industries generate wastes, some of which may be considered hazardous because of the presence of toxic organics and heavy metals (Obot *et al.*, 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 kinds of pollutants affect human beings 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 occur 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.

Treated 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, as a result of poor maintenance of installed wastewater treatment facilities and management's wrong attitude towards environmental management 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).

Industrial effluents vary in their levels of toxicity depending on the nature of operational activities and the effectiveness of the wastewater treatment facility in the industry. One approach to assessing the potential hazards involves determinations of various possible effluents being discharged into the main water bodies of the environment (Perry *et al.*, 1978).

Several investigations have shown positive correlation

between petroleum based industrial pollutions and the health of aquatic organisms. Another observation suggested a positive 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).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.

To reduce the risk of pollution, 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 petroleum based industrial sites selected for these studies were coded: KP, TL, OL(I) and OL(II).

The effluent treatment plant available in OL and TL facilities is the oil - water separator pits, which separates oil from water by gravity as the mixture of oil in water flows from inlet to outlet within the pit (designed to American Petroleum Institute standard). The separated oil which floats on top of water is then mechanically skimmed off and the water is allowed to flow into the final chamber. At this time, concentration of oil and grease, and other parameters being monitored, 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).

Mohammed *et al.,* (2013), determined the concentrations of benzene and phenol in in some petroleum based industrial effluents in Kaduna metropolis Nigeria, and the results showed that benzene concentration range was 0.48 ppm to 0.59 ppm and phenol concentration range was 3.84 ppm to 4.13 ppm. Both compounds were present at higher concentrations than the USEPA acceptable limits (0.2 ppm).

Oxirane and naphthalene are other organic compounds which are considered carcinogenic to human and other animals. Oxirane has strong alkylating properties and this makes it a universal poison for protoplasm as it causes clotting of proteins, deactivation of enzymes and other biologically important components of a living organism (NPI, 2009). Chronic exposure to oxirane is also mutagenic. Oxirane is classified in group 1 (known to be human carcinogen), while naphthalene is in group 2B (possibly carcinogenic to humans) by the International Agency for Research on Cancer (IARC), (IARC, 2011). The national toxicology program (NTP) and the national pollution inventory (NPI) also identified oxirane as a known human carcinogen (NTP, 2011; NPI, 2009).

This paper assessed the concentration of oxirane and naphthalene in the effluents discharged into the environment from four selected petroleum based industries within Kaduna metropolis of Nigeria coded as OL(I), OL(II), TL and KP. The concentration of these pollutants were compared with united state environmental protection agency (EPA) maximum permissible limits.

Experimental

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$_2$SO$_4$) 50 %, methylene chloride (CH$_2$CL$_2$) (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 and August 2012, at Nigerian Defence Academy, Kaduna and National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria.

Sampling

Samples were collected from effluent channels from KP, OL(I), OL(II) and TL. 1000 cm^3 of the wastewater was sampled from each 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 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 (Mohammed *et al.*, 2013).

Extraction

1000cm^3 of the sample was transferred quantitatively into a cleaned and dried separatory funnel. The pH of the sample

Table 1. Concentration of oxirane in both acid and base extracts of the various samples.

Sampling stations	Concentration of oxirane (ppm) in acid extracts				Concentration of oxirane (ppm) in base extracts			
	morning	afternoon	evening	Average in acid	morning	afternoon	evening	Average in base
OL(I)	ND	ND	ND	ND	ND	ND	ND	ND
OL(II)	4.9	ND	7.02	5.96	8.49	7.48	5.86	7.28
TL	ND	8.11	ND	8.11	ND	6.98	ND	6.98
KP	6.99	2.88	ND	4.94	5.92	8.40	ND	7.16
EPA limit				<1				<1

Table 2. Concentration of naphthalene in both acid and base extracts of the various samples.

Sampling stations	Concentration of naphthalene (ppm) in acid extracts				Concentration of naphthalene (ppm) in base extracts			
	morning	afternoon	evening	average	morning	afternoon	evening	average
OL(I)	ND	ND	ND	ND	ND	0.47	ND	0.47
OL(II)	ND	ND	ND	ND	ND	ND	ND	ND
TL	ND	ND	ND	ND	ND	ND	ND	ND
KP	ND	ND	ND	ND	ND	ND	0.51	0.51
EPA limit				<1				<1

Table 3. Sum of the concentrations of oxirane and naphthalene in acid and base and average values for the various sampling sites.

Sampling stations	Concentration of oxirane (ppm)				Concentration of naphthalene (ppm)			
	morning	afternoon	evening	average	morning	afternoon	evening	average
OL(I)	ND	ND	ND	ND	ND	0.47	ND	0.47
OL(II)	13.39	7.48	12.88	11.25	ND	ND	ND	ND
TL	ND	15.09	ND	15.09	ND	ND	ND	ND
KP	12.91	11.28	ND	12.10	ND	ND	0.51	0.51
EPA limit				<1				<1

was adjusted to more than 11 with 10 mol/dm³ sodium hydroxide solution. Methylene chloride (60cm³) was added to the pH-adjusted content in the separatory funnel and extracted by shaking the funnel for two minutes with 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 250cm³ 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 cm³ 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. This procedure was repeated for all the samples which were prepared and kept for GC-MS analysis.

Results and Discussion

The concentrations of oxirane and naphthalene detected in the samples in both the acid and the base extracts are reported in Tables 1 and 2 respectively.

The Average concentrations of oxirane and naphthalene detected in the samples are reported in Table 3.

From Table 1, oxirane was not detected in all the sample from OL(I) in both acid and base extracts.

In OL(II), oxirane was detected in the acid as well as the base extracts of the morning samples with concentrations 4.9ppm and 8.49ppm respectively. In the afternoon samples, oxirane was not detected in the acid extract, but was detected in the base extract with concentration 7.48ppm. while in the evening samples, it was detected in both the acid and base extracts with concentrations 7.02ppm and5.86ppm respectively.

Oxirane was not detected in the morning and evening samples from TL in both acid and base extracts. In the afternoon samples however, oxirane was detected in both

acid and base extracts with concentrations 8.11ppm and 6.98ppm respectively, implying that oxirane was extractable in both acidic and basic medium.

In samples collected from KP, oxirane was detected in the acid and base extracts in the morning samples with concentrations 6.99ppm and 5.92ppm respectively. Oxirane was also detected in the afternoon samples in both acid and base extracts with concentrations 2.88ppm and 8.40ppm respectively. It was however not detected in both extracts of the evening samples, indicating that oxirane may not be present in the effluent at the time of sampling in the evening.

In all cases, oxirane concentrations were found to be higher than the United State Environmental Protection Agency (USEPA) acceptable limit. From Table 2, naphthalene was not detected in the acid extracts of all the samples from OL(I). It was also not detected in the base extract of the morning and evening samples from OL(I), but was however detected in the base extract of the afternoon sample with concentration 0.47 ppm.

In all the samples from OL(II) and TL, naphthalene was not detected in both the acid and base extracts.

Naphthalene was not detected in the acid extracts of all the samples from KP. It was also not detected in the base extracts of the morning and afternoon samples, either because naphthalene was not present or the concentration was below detection, but was detected in the evening sample with concentration 0.51 ppm. It can be seen from Table 2, that the concentration of naphthalene is within the USEPA acceptable limit.

Naphthalene is the simplest polycyclic aromatic hydrocarbon with characteristic odour that is detectable at concentrations as low as 0.08ppm by mass (Fern, 2007). Available data for naphthalene indicate that acute and chronic toxicity to freshwater aquatic life occur at concentrations as low as 2.3 ppm and 0.62 ppm respectively, and would occur at lower concentrations among species that are more sensitive (Fern,2007). Naphthalene is classified in "group 2B" (possibly carcinogenic to humans) by IARC. This means that there is sufficient evidence of carcinogenicity of naphthalene from animal studies. Table 3 shows the sum of the concentrations of the compounds in acid and base in the morning, afternoon and evening respectively in each sampling station.

From Table 3, oxirane was not detected in the morning, afternoon and evening effluent samples collected from OL (I). Naphthalene was not detected in the morning and evening samples but was detected in the base extract of the afternoon samples with concentration 0.47 ppm.

In the effluent samples from OL (II), oxirane was detected in the base (8.49 ppm) and acid (4.9 ppm) extracts of the morning samples (Table 1), with a total concentration of 13.39 ppm. In the afternoon samples it was detected only in the base extract with concentration of 7.48 ppm and in the evening samples it was detected in both the base and acid

extracts with a total concentration (12.88 ppm). Naphthalene was not detected in any of the samples.

In the samples collected from TL, oxirane was not detected in the morning and evening samples but was detected in the base and acid extracts of the afternoon samples with total concentration (15.09 ppm). Naphthalene was not detected in the morning, afternoon and evening samples.

In the samples collected from KP, oxirane was detected in both base and acid extracts of the morning and afternoon samples with total concentrations 12.91 ppm and 11.28 ppm respectively. It was however, not detected in the evening samples. Naphthalene was not detected in the morning and afternoon samples, but was detected in the base extract of the evening samples with concentration 0.51 ppm.

The average concentration of oxirane in OL (II) (11.25 ppm), TL (15.09 ppm) and KP (12.10 ppm) were higher than the permissible limit (<1 ppm).

The average concentration for naphthalene in OL (I) (0.47 ppm) and KP (0.51 ppm) were within the permissible limits (<1 ppm).

It has been reported that there is relative proportions of oxirane and propylene oxide in lubricating oils which play some significant roles in some lubricant properties such as pour point, water solubility and pressure-viscosity relationship (Brown et al., 2010). Price and Jayjock (2008) had also reported that premium motor spirit (PMS), automotive gas oil (AGO) ,fuel oil and lubricants contain an average weight of 0.25%, 0.26%, 0.22% and 0.059% of naphthalene respectively. The presence of oxirane and naphthalene in the effluents of these industries may partly be due to the stains of these products on the floor of the industries, which are washed off using degreasers.

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

In conclusion, this study has shown that effluents from the selected petroleum based industries contain oxirane and naphthalene. While naphthalene concentration in the effluents is within acceptable limit, oxirane which is classified as a human carcinogen is present at concentrations higher than acceptable limits in the effluents being discharged into the environment from these industries, indicating an enrichment of pollution load of the environment. This study is the first of its kinds in providing information on possible presence of oxirane and naphthalene as carcinogenic organic compounds in industrial effluents in Kaduna state. It is recommended that appropriate measures for control of carcinogenic organic

compounds in industrial effluents be put in place for the industries in view of the devastating effect of toxic organic compounds on animals, plants and aquatic life.

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