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Preliminary Studies on Produced Water from Obigbo-North Oil Field of Niger Delta, Nigeria

Leo C Osuji[1,2,3]* and Boma Brown-Harry[1]

[1]Petroleum and Environmental Chemistry Research group, Department of Pure and Industrial Chemistry, University of Port Harcourt, East-West Road, Choba, PMB 5323, Port Harcourt, Nigeria

[2]World Bank Africa Centre of Excellence for Oilfield Chemicals Research, University of Port Harcourt, Choba, PMB 5323, Port Harcourt, Nigeria

[3]Institute of Natural Resources, Environment and Sustainable Development (INRES), University of Port Harcourt, Choba, PMB 5323, Port Harcourt, Nigeria

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***Corresponding author:** Leo C Osuji, World Bank Africa Centre of Excellence for Oilfield Chemicals Research, University of Port Harcourt, Choba, PMB 5323, Port Harcourt, Nigeria

ABSTRACT

Produced water from Obigbo North oilfield in the Niger Delta region of Nigeria was analyzed for hydrocarbons and heavy metal concentrations, with a view to determining an appropriate technique for remediation. Oilfields in this region are known to have high water-to-oil ratio ranging from 50% to 95% water content, due to its secondary and tertiary production phases Detectable amounts of polycyclic aromatic hydrocarbons (PAHs), benzene, toluene, ethyl benzene and xylene (BTEX) compounds and heavy metals (Cd, Pb, Cr, Cu Fe, Ni) were measured. Despite the low concentration of BTEX compounds, disposal into the aquatic environment would pose a major life hazard to aquatic organisms and consequently to human beings living in that area. Therefore, best available treatments methods should be studied and put in place in order to prevent the possibility of having this unwanted occurrence and the like, these treatment methods should therefore be able to completely remove the high molecular weight PAHs compounds so also be able to maintain the absence of BTEX compound in the produced water.

Keywords: Produced water; hydrocarbons; oil and gas; heavy metals; PAHs; BTEX

Introduction

Produced water is a by-product of the production of oil and gas hydrocarbons from underground reservoirs. Water is naturally present in these reservoirs and, despite all efforts to produce the hydrocarbons selectively, some water is still produced, either admixed as a liquid with the oil or as vapour in the hydrocarbon gas. When the hydrocarbons are eventually produced, the water component is separated from the oil and gas in the first stages of processing. For offshore operations, the separated produced water is generally known to be discharged into the sea. However, a small proportion of the hydrocarbons is found dissolved in the separated water as a result of their inherent solubility. Different hydrocarbon compounds have different solubilities in water; aromatic hydrocarbons are relatively more soluble than aliphatic hydrocarbons. Thus, the produced water usually contains more of the light aromatic hydrocarbons, in addition to the suspended oil droplets[1-3].

Generally, the chemical composition of produced water may vary over a wide range depending on attributes of the reservoir's geology and its production lifetime. In addition to the naturally occurring dispersed oil and aromatics, typical produced water may also contain dissolved organic acids, phenols, inorganic compounds and some traces of chemicals added in the production/separation line[4]. Produced water from oil production fields differs from that from gas production fields. Water from gas production fields generally has a higher content of low molecular weight aromatic hydrocarbons, such as BTEX (benzene, toluene, ethyl benzene and xylene), than water from oil production platforms. However, the total amount of water produced from gas fields is much smaller than the quantity from oil production fields. While many gas fields discharge less than 10m3 of produced water per day, most oil fields discharge hundreds or even thousands of m3 of produced water per day, however, the quantity of produced water in a reservoir change during the lifetime of the oil field.

Treatment processes for separation of oil and water before discharge have until now been based on the use of gravitational force, utilizing the difference in specific gravity between oil droplets and water. The oil droplets will generally float to the top of the water phase where they can be removed. Gravity treatment methods are not able to remove dissolved hydrocarbon components. At wastewater treatment plants at refineries or other facilities dealing with significant quantities of hydrocarbons, biological treatment (breakdown by micro-organisms) is the best means of breaking down and removing the dissolved hydrocarbons. This option is not available at offshore oil and gas installations.

Abdelhamid, et al. have reviewed recent bg technologies in the treatment of produced water[5]. Other contemporary authors have similarly reported recent advances in the treatment of oilfields produced water[6-8]. In their own view Alomar et al., 2022 recommended the use of adsorption and advanced oxidation processes. Given the quantum of the generated produced water as well as the limited availability of fresh water for aquaculture and irrigated farming, there is a need for the recycling of produced water for use as process water in chemical industries as well as for the possible use in agricultural irrigation. This requires a comprehensive treatment of produced water for its safe reuse. Recycling of produced water for use in process industries is imperative because it will reduce the negative impact of these pollutants on aquatic, public health as well as promote the environmental integrity of water resources[9].

Clearly, produced water has the potential to contaminate its receiving environment, especially in an offshore setting. It is our interest in the present preliminary investigation to evaluate the aromatic and heavy metal components of the produced water from Obigbo-North, an indigenous oil field in Niger Delta, Nigeria. Oilfields in this region are known to have high water-to-oil ratio ranging from 50% to 95% water content, due to its secondary and tertiary production phases[10]. The oilfield for the present study consists of many oil producing wells located in an ecologically viable environment of dual commercial interest, an environment grappling with the conflict of oil exploitation and agricultural productivity.

Materials and Methods

Geo-characteristic description of Study area

The study area is in Oyigbo LGA of Rivers State of Nigeria. The LGA is made up of towns, villages and districts such as Obeama, Azusogu, Okoloma, Umuosi, Mgboji, Egberu, Okponta, Afaukwu and Ndoki. The current estimated population of Oyigbo LGA is put at 209,841 inhabitants. Oyigbo LGA is rich in deposits of crude oil and natural gas with the area hosting several oil corporations which contribute to the economy of the area. The LGA is a hub for fishing with the rivers and tributaries that constitute the area's hydrosphere being rich in seafood. Other important economic activities in Oyigbo LGA include farming, trade and crafts making. Oyigbo LGA has an average temperature of 25 degrees Celcius with the area hosting several rivers and tributaries. The average humidity level in the LGA is 79 percent while the average wind speed in the area is put at 12 km/h. **(Figure 1)** contains map of the study area.

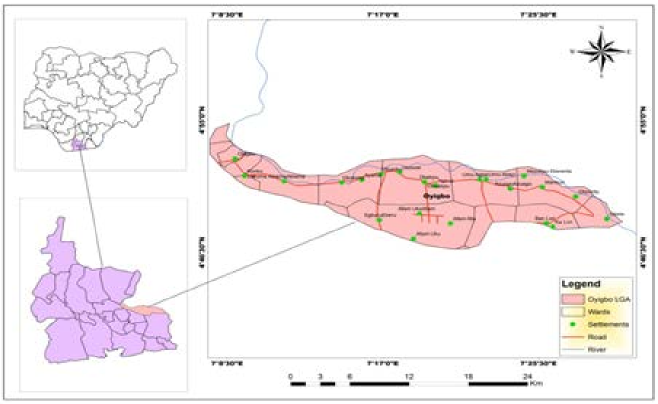

Figure 1: Location Map of study Area.

Source of produced water samples

Produced water samples were obtained from three oil producing wells in Obigbo North oil field of Niger Delta Nigeria. Obigbo North oil field is located in the eastern part of the Niger Delta region of Nigeria. The area was one of the British Oil Rivers Protectorates from 1885 until 1893, when it was expanded and became the Niger Coast Protectorate. The area is densely populated with some of the people engaged in farming and oil palm production.

Liquid-liquid extraction

One milliliter (I ml) of the sample was measured into a 10ml volumetric flask and made up to mark with the extracting solvent which was pentane and then shaken vigorously. The mixtures were allowed to concentrate to 1ml at room temperature and then transferred into the chromatographic column for clean-up/separation.

Sample clean-up/separation

1cm of moderately packed glass wool was placed at the bottom of 10mm, I.D X 250mm long Chromatographic Column after which a slurry of 2g activated silica gel in 10ml methylene chloride was prepared and placed into the chromatographic column. To the top of the column was added 0.5g of sodium sulphate, the column was then rinsed with an additional 10ml of methylene chloride. After which it was pre-eluted with 20ml of pentane; this was allowed to flow through the column at a rate of about 2 minutes until the liquid in the column was just above the sulphate layer. Immediately, 1ml of the extracted sample was transferred into the column, the extraction bottle was rinsed with 1ml of Pentane and added to the column as well. The stop-cock of the column was opened and the eluant was collected with a 10ml graduated cylinder.

Just prior to exposure of the sodium sulphate layer to air, pentane was added to the column in 1-2ml increments. Accurately measured volume of 8-10ml of the eluant was collected. This was labeled “ALIPHATICS”. Following the recovery of “ALIPHATIC” fractions and just prior to exposure of the sodium sulphate layer, the column was eluted with 1:1 mixture of Acetone and methylene chloride in 1-2ml increments and another accurately measured 8-10ml of the eluant was collected and was labeled “AROMATICS”. The “AROMATIC” fraction was concentrated to 1ml for PAHs and BTEX analyses using Gas Chromatography.

Gas chromatographic (GC) analysis

The concentrated “AROMATIC” fractions were transferred into labeled Glass Vials with Teflon Rubber Crimp caps for analysis; 1µl of the concentrated sample was injected by means of hypodermic syringe through a rubber septum into the column and separation occured as the vapor constituent partition between the gas and liquid phases. The sample was automatically detected as it emerges from the column (at a constant flow rate) by the FID detector whose response is dependent upon the composition of the vapor, by measuring the retention time (i.e. the minutes between the time the sample was injected and the time the Chromatographic peak was recorded).

Analysis for heavy metals

Fifty millilitres (50ml) of the produced water sample were measured into a beaker. Aqua regia solution (i.e. 2ml of HNO3(aq) + 6ml HCl(aq)) was added into the sample and the resulting solution was heated to near-dryness using a hot plate. The solution was filtered through a filter paper into a 50ml volumetric flask and made up or diluted to mark with distilled water. The sample was thereafter analyzed using the Atomic Absorption Spectrophotometer (AAS GBS AVANTA VERSION 2.02), according to the following respective standards and individual metal absorption wavelengths:

Cu-standards: - 1mg/l and 3mg/l Cu in aqueous solution.

Wavelength: -324.7nm
Fe-standards: -1mg/l and 3mg/l Fe in aqueous solution.
Wavelength-248.3nm
Ni-standards: -2 mg/l and 6 mg/l in aqueous Ni solution
Wavelength-232.0nm
Cr –standard: -10 mg/l and 28 mg/l Cr in aqueous solution
Wavelength-228.8nm
Cd- standards: -1mg/l and 2 mg/l Cd in aqueous solution
Wavelength-228.8nm
Pb-standards: -2 mg/l and 4 mg/l Pb in aqueous solution
Wavelength-217.0nm

Results and Discussion

Polycyclic Aromatic Hydrocarbons (PAHs)

Highlights of the polyaromatics (PAHs) in the produced/injection water contained in **(Table 1)**. The result shows that 1,2-Benzanthracene, with a mean value of 129 mg\l, was present in highest concentration, while Indeno (1,2,3-cd) pyrene had the least mean concentration of 1.2 mg/l. 1,2,5,6-Dibenzathracene and 1,12-Benzoperylene were not detected (cf: Table 1). The PAH profile shows a substantial decrease in the number of PAHs present in the produced water with increasing molecular weight of the compounds therein. Although Benzo(b)fluoranthene and Benzo(k)fluoranthene are not predominant, their mere presence can cause high toxicity. Though they are known to be insoluble in water, they form an oil-in-water emulsion, which can be ingested by fishes and other filter-feeding organisms. Besides, most high molecular weight PAHs have been widely reported to be carcinogenic[11].

The distribution of PAHs in the samples under investigation showed higher concentrations for naphthalene, acenaphthene 1,2-benzanthracene and very low values for PAHs such as pyrenes, Indeno (1,2,3-cd) pyrene, benzo (a) pyrene etc. Compounds like naphthalene, acenaphthene and 1,2-benzanthracene are of lower molecular weight when compared with PAHs like pyrenes, Indeno (1,2,3-cd) pyrene, benzo (a) pyrene, which are high molecular weight. The low molecular weight PAHs are known as fossil PAHs, while the high molecular weights are known to be pyrolytic. The dominance of the low molecular weight PAHs suggests that they are not produced through combustion of hydrocarbons, but as components of fossil fuel or petroleum. The low molecular weight PAHs are harmful to living organisms because they can penetrate more easily into their cell membrane than the high molecular weight (HMW) PAHs. But they are still less harmful than the HMW PAHs because they are susuptible to secondary processes (such as weathering and biodegadation), unlike the HMW PAHs that can bioaccumulate in living cells and the environment because of their resistance to biodegradation[12].

Generally, the absence of BTEX compounds from the samples of produced water under test **(Table 2)**, as well as the predominance of three ring PAH compounds shows that the produced water samples might be a blend of a weathered crude oil. Produced water obtained from weathered crude oil, as compared with produced water from neat fresh crude oils, is less toxic to aquatic organisms. BTEX compounds are generally acutely toxic to aquatic organisms together with high molecular weight PAH compounds, but since they are both below detection limits in the present analysis, one is tempted to infer in the alternative that the produced water under test might be less toxic when compared to similar samples from neat crude oils. However, the higher molecular weight PAH compounds that were minutely detected in the test might undergo bioaccumulation after a long and constant discharge and this might result to an increase in its toxicity[13,14,12].

Table 1: Hydrocarbon types and distribution in the produced water.

Hydrocarbons	Amount (Mg/l)			
PAH TYPE	**S1**	**S2**	**S3**	**Mean**
Naphthalene	38.105	22.709	28.864	29.893
Acenaphthylene	37.517	11.778	16.388	38.561
1,2-Benzanthrcene	150.081	219.049	18.489	129.206
Acenaphthene	24.549	8.589	27.754	20.964
Fluorine	26.862	25.499	20.639	24.333
Phenanthrene	35.426	13.802	12.415	20.548
Anthracene	46.575	9.188	43.396	33.053
Fluoranthene	18.730	17.802	21.061	19.183
Pyrene	58.328	2.785	9.841	13.651
Benzo (a) anthracene	119.124	3.349	11.459	44.674
Chrysene	19.638	12.442	2.776	11.619
Benzo (b) fluroanthene	26.642	4.079	4.352	11.691
Benzo (a) Pyrene	9.597	3.088	$9.097x10^{-1}$	4.532
Indeno (12,3-d) pyrene	2.113	1.353	$3.004x10^{-1}$	1.255
Dibenzo(a,h) anthracene	4.102	2.694	6.83510^{-1}	2.493

Table 2: BTEX Analysis Result.

Hydrocarbons	Amount (Mg/L)		
Benzene	< 0.5	< 0.5	4.90
Toluene	< 0.5	< 0.5	5.70
Ethyl benzene	< 0.5	< 0.5	5.98
p-xylene	< 0.5	< 0.5	8.36
m-xylene	< 0.5	< 0.5	8.59

Although further investigation is needed to empirically quantify the quantal responses of aquatic organisms to lethal doses of the produced water samples, data obtained from this preliminary investigation seem to corroborate the reports of many past works on the impact of PAHs in hydrocarbon containing water. For instance, throughout the 1990s, evidence accumulated that produced water might be less benign than it appeared; for instance, a 1992 conference on produced water showed clear effects of the toxic hydrocarbon contents of oil-in-water contamination on sea urchins[15]. Further, Ogali, et al, reported possible systemic effects of PAHs from spent Lubricating oil on the Afican catfish, Clarias gariepinus[2]. HMW PAHs were reported to be resistant to degradation and could illicit substantial toxicity in both aquatic and terrestrial environment. Polycylic aromatic hydrocarbons have also been detected in the livers of some sea mammals like the otters. Naphthalene, Fluorene, Phenanthrene, anthracene and acenapthylene were the predominant compounds found in the livers of the otters[16]. It was also reported that in shallow, turbid waters, elevated concentrations of hydrocarbon were detected in sediments up to about 1000m from discharge; the aromatic hydrocarbons and metals detected the in produced water were found to be toxic[17]. Judging from the evidence of the data obtained in this study where these PAHs were found in predominant concentration, the produced water from the Obigbo North field might be substantially harmful to such aquatic organisms, especially if discharged into an offshore environment. **(Figure 2)** contains the distribution signatures of these polyclic aromatic hydrocarbons.

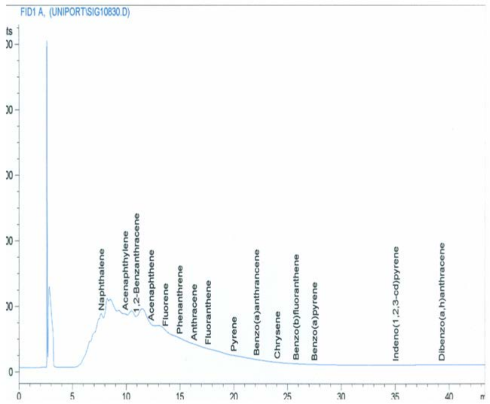

Figure 2: Chromatogram showing the distribution of the polyclic aromatic hydrocarbons.

Heavy Metals

The Results of the heavy metal analysis are collected in **(Table 3)**. Heavy metals are those metallic chemical elements with relatively high densities, usually greater than 5g/cm3 and are toxic or poisonous at low concentrations. The concentrations of heavy metals in the analyzed produced water showed negligible amounts of Cd, Pb and Cr while that of Fe and Ni are beyond tolerable limits set by the Nigerian Upstream Petroleum Regulatory Commission (NUPRC). Cu and Ni showed concentrations within the acceptable limits.

High concentration of iron in the environment has been found to be very hazardous to human begins. It has been reported that human body absorbs iron in animal products faster than that in plant products. If it contacts with the tissues, it remains there without being degraded. Iron may cause conjunctivitis, choroiditis and retinitis. Iron is known to bioaccumulate and is also persistent in the environment. 1.814mg/l of iron the produced water means that the water should be treated further before discharging into the sea. Nickel having 0.143 is far above the regulatory limit of NUPRC in produced water, the discharge of this produced water into the sea may cause nickel accumulation. Having <0.001 shows that there is no danger of pollution from Cd, Pb and Cr.

Table 3: Result of the Heavy Metals Analysis.

Metal (mg/L)	Sample (1)	Sample (2)	Sample (3)	Sample value
Cd	01001	01001	01001	01001
Pb	<0.001	<0.001	<0.001	<0.001
Cr	<0.001	<0.001	<0.001	<0.001
Cu	0.025	0.023	0.018	0.022
Fe	1.864	1.810	1.769	1.814
Ni	0.191	0.110	0.129	0.143

The presence of detectable levels of the analysed heavy metals (cf: Table 3) suggest pollution of the water-sediment column. It has been shown that sediments that reside at the bottom of the water column play a major role in the pollution scheme of the river systems by heavy metals. These heavy metals can be released back to water column by changes in environmental conditions, like the presence of organic chelators

Studies carried out by Kakulu and Osibanjot showed high levels of Pb, Cr, Ni, V and Zn in Port Harcourt and Warri sediment which suggests that effluent emanating from oil companies and refineries situated in these places have led to the heavy metal pollution of the aquatic environments[18]. Similar intoxication by heavy metals has been widely reported in literature[19]. For instance, Fahmy studied the distribution of dissolved and particulate heavy metals in water column of the Damietta branch of the River Nile. Studies show that there was a direct relationship between levels of metals in the lake water and in tissues of fish. Generally, heavy metal contamination in water and soil presents a growing global issue that poses significant risks to environmental integrity and human well-being. Various heavy metals, including arsenic (As), lead (Pb), mercury (Hg), cadmium (Cd) and chromium (Cr), contaminate ecosystems. Given the severe effects of heavy metals, urgent actions are required to eliminate them from the ecosystem[20,21].

Conclusion

Despite the low concentration of BTEX compounds, disposal into the aquatic environment would pose a major life hazard to aquatic organisms and consequently to human beings living in that area. Therefore, best available treatments methods should be studied and put in place in order to prevent the possibility of having this unwanted occurrence and the like, these treatment methods should therefore be able to completely remove the high molecular weight PAHs compounds so also be able to maintain the absence of BTEX compound in the produced water. The BTEX and PAHs can be removed by an extraction process involving the addition of an immiscible solvent in the solution that will absorb the solute (in this case the aromatics) because of their higher affinity towards the extraction solvent. A gas condensate can be injected to act as an extraction-solvent. The solvent extracts the dissolved hydrocarbons from the water phase and these are then removed in the hydro cyclone.

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