Physiochemical And Microbial Qualities Of Petroleum Sludge

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Abstract: The physiochemical and microbial qualities of petroleum sludge freshly collected from the facilities of petroleum exploration and Production Company of Nigeria, in Rivers State, Niger Delta was investigated. Analysis of the petroleum sludge indicated that the petroleum sludge was acidic with pH value of 5.82, a high total petroleum hydrocarbon (TPH) content of 38,993.2mg/l made up of mainly between 10-40 carbon unit compounds. It also recorded high biochemical oxygen demand (BOD) and chemical oxygen (COD) of 448.0 and 1,900 mg/l respectively. The mean values of salinity, nitrate, phosphate and sulphate were 3,249.0, 10.59, 0.98 and 18.58mg/l respectively. Conductivity had a high value of 5, 230.0 $\mu s/cm$ and salinity was 3,249.0mg/l. From the analysis of heavy metal of the sludge, iron (Fe) recorded a high concentration of 494.22mg/l in relation to zinc, copper, vanadium, nickel and lead that were 3.791, 3.329, 0.910, 4.537 and 2.590mg/l respectively. The total heterotrophic bacterial (THB) and total fungal (TF) counts were $2.5x10^6$ cfu/ml and $2.0x10^3$sfu/ml respectively while the hydrocarbon utilizing bacterial (HUB) and hydrocarbon utilizing fungal (HUF) counts were $2.0x10^3$ cfu/ml and $2.0x10^3$sfu/ml respectively. These values exceeded the World Health Organization (WHO) standard for potable water. This shows that the petroleum sludge has high pollution potential and therefore must of necessity be treated before disposal into the recipient environment. The COD; BOD ratio was 3.60 which indicate that the sludge can undergo biodegradation and further suggests that biological method (bioremediation) could be used in treatment of the sludge.

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1. Introduction

The exploration, production, refining and distribution activities of petroleum industries results in the generation of a considerable volume of waste oily sludges. The oily sludges comes from a variety of sources including storage tank bottoms, oily-water separators, dissolved air floatation units, cleaning of processing equipment, pipeline and flow station facilities clean up in the oil and gas industry (API, 1991; Manning and Thompson, 1995, McMillen *et al.*, 2004; Adoki and Orugbani, 2007; Ayotamuno *et al., 2007*) Formation of petroleum sludge is attributed to two major factors; which include the inorganic residues (sediments, sand, scales and dust) and the precipitation of paraffinic wax in crude oil. The reason behind wax precipitation is temperature changes. In addition to the above reasons, the oxidation of heavy organic material in crude oil due to climate changes or from oxidizing bacteria and fungai (Manning and Thompson, 1995).

Petroleum sludge contains toxic substances like aromatic hydrocarbons (Benzene, toluene, ethyle, benzene and xylene), polycyclic aromatic hydrocarbons (PAHs) (Swoboda-colberge, 1995) and high total hydrocarbon content (Ayotamuno *et al.*, 2007). The effects of these pollutants in the oil/gas producing communities involves; loss of aesthetic values of the natural beaches, damage to marine wild life, modification of ecosystem through species elimination, delay in flora and fauna succession and decrease in fishery resources (Reed and Johnson,1995; Atuanyan and Tudararo-Aherobo, 2015).

The occurrence of hydrocarbon pollutants in the aquatic and terrestrial environments is of international concern due to their persistence toxicity and bioaccumulation in the lipid tissue of aquatic biota (Dokaniakis, 2005). Petroleum sludge disposal is a worldwide environmental problem. Large volumes of petroleum sludge generated in the petroleum industry need to be analyzed or characterize and disposed off in an environmentally safe manner.

This study was aimed to characterize the physicochemical and microbial qualities of petroleum sludge from the crude oil processing plant located at Obegi community in Ogba/Egbama Ndoni Local Government Area of Rivers State, Nigeria and compare the values obtained with the Department of Petroleum Resources (DPR) Limits (DPR, 2002) and World Health Organization (WHO) Standards (WHO, 1971) for potable water in order to assess the general level of pollution potentials of the petroleum sludge sample being investigated.

2. Materials And Methods

2.1. Sample collection

The petroleum sludge sample was obtained from Obegi oil Processing Plant located at Obegi in Ogba/Egbama Ndoni Local Government Area of Rivers State, Nigeria. Sludge samples were directly collected from different outlet valves of sludge vessels when the plant was operational (life plant), and mixed together to form a composite sample which was collected into two sterile big glass bottles and covered. The sludge sample was transported in Ice Park to the laboratory for analysis. Sample was preserved in the refrigerator at 4^{o}c when not in use. All the reagents employed for this study were of analytical grade and were obtained from BDH Chemicals Limited Poole England. Nutrient agar (NA) and potato dextrose agar (PDA) were obtained from international diagnostic group, England. Filter paper (Whatman No.1) was obtained from WER Bauston Limited.

2.2. Physicochemical Analysis

All physicochemical characteristics analyzed were carried out as described in the standard methods for the examination of water and wastewater (APHA, 1998) and methods adopted from Stewart *et al.*, (1974). For TPH, Gas Chromatogram Flame Ionization Detector (FID) was employed (USEPA, 1996) 3630C HP5890 series II GC. Total hydrocarbon content (THC) was determined using a SHIMADZU infrared spectrophotometer according to ASTM (1999) method D3921. Protocols for presence of heavy metals in the sludge sample were by use of GBC AVANTA atomic absorption spectrophotometer (AAS).

2.3. Enumeration of Microbial Populations

The bacterial and fungal culture was carried out by serial dilution of the sludge sample. The THB count of petroleum sludge sample was performed on NA (oxoid) in duplicates using spread plate method (APHA, 1998). The HUB count was carried out in duplicates on mineral salt agar (MSA) of Mills *et al.*, (1978) as modified by Okpokwasili and Odokuma (1990). The total fungal (TF) count was estimated by plating 1ml of serial dilution on PDA plates in duplicates. Approximately 10ml of 10% lactic acid was added to inhibit bacterial growth. Incubation was at 30^{o}C for 5-7 days. The same technique was employed for HUF counts. Sterile filter papers (Whatman No.1) saturated with Bonny light crude oil were aseptically placed on the inside lid of each plate and kept in an inverted position for both HUB and HUF counts and incubated accordingly for bacterial and fungal growths. Enumeration of plates was carried out after incubation periods.

3. Results

The results of the physiochemical and heavy metal analysis of petroleum sludge sample are presented in Tables 1 and 2 while Table 3 shows the Department of Petroleum Resources (DPR) limit for some of the parameters. Bacterial and fungal counts of Petroleum Sludge Sample is shown in Table 4 while Total Petroleum Hydrocarbon (TPH) of test oily sludge (sample from G.C. result) is shown in Figure 1.

Table 1: Physicochemical characteristics of petroleum sludge sample.

Sludge characteristics	Unit	Values
pH	-	5.84
Salinity	mg/l	3,249.0
Conductivity	µs/cm	5,230.0
Alkalinity	-	1,900.0
BOD	mg/l	448.0
COD	mg/l	1,600.0
Nitrate	mg/l	10.59
Sulphate	mg/l	18.58
Phosphate	mg/l	0.98
THC	mg/l	915.0
TPH	mg/l	38,993.2

Table 2: Heavy Metal Load of Petroleum Sludge Sample

Parameter	Value (mg/l)
Iron (Fe)	494.22
Zinc (Zn)	3.791
Copper (Cu)	3.329
Vanadium (V)	0.910
Nickel(Ni)	4.537
Lead (Pb)	2.590

Table 3: Department of Petroleum Resources (DPR) Limits for some parameters

Parameter	DPR Limits
pH Maximum	8.5
pH Minimum	6.5
Temperature	35oC
Turbidity	10.00NTU
TSS	60.00mg/L
Salinity	600.00mg/l
Oil and Grease	10.00mg/l
COD	40.00mg/l
BOD	10.00mg/l
Cr5+	0.03mg/l
Total Fe	1.00mg/l
CU2+	1.00 mg/l
Zn2+	1.50 mg/l
Pb2+	0.05 mg/l

Source: (DPR, 2002).

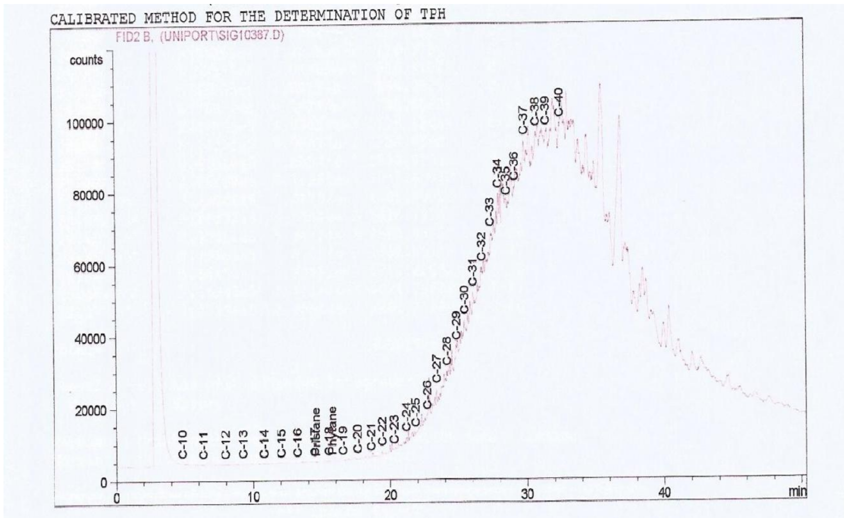

Fig. 1: Total Petroleum Hydrocarbon (TPH) of Test Oily Sludge (Sample from G.C. Result)

Table 4: Bacterial and Fungal Counts of Petroleum Sludge Sample

Type of Count	Value
THB	2.5x106 cfu/ml
HUB	2.0x105 cfu/ml
TF	2.0x105 sfu/ml
HUF	2.0x105 sfu/ml

4. Discussion

From the results, the pH value for the fresh petroleum sludge was 5.84. This indicates that the sludge is acidic. Studies have shown that low pH is toxic to fish and other aquatic lives, Atuanyan and Tudararo-Aherobo, 2015). Similar low pH level of petroleum sludge had been observed by Atuanyam and Tudarao Aherobo (2015) where they recorded low pH of 5.81 and a pH of 5.48 by Asia *et al*., (2007). The salinity value of the sludge (3,249mg/l) was very high compared with the DPR limits of 600mg/l. The BOD, COD and THB count were 448mg/l, 1600mg/l and 2.5x10^{6}cfu/ml respectively. These values are quite higher when compared to DPR limits and WHO standards. These indicate strong pollution potentials and therefore, need for biotreatment of sludge is necessary before disposal.

The result also shows that the ratio of COD: BOD was 3.60. This indicates that the sludge is capable of undergoing substrate biodegradation. Similar observation was made by Asia *et al*., (2006) where they recorded the ratio of COD: BOD of petroleum sludge to be 2.60. The enumeration of high population of THB, (2.5x10^{6}cfu/ml) and 2.0x10^3 cfu/ml for both HUB and HUF respectively is an indication that the sludge sample could be degraded by the hydrocarbon utilizing microorganisms (Okerentugba and Ezeronye, 2003; Ojo, 2006). On the other hand, the high value of COD indicates a high potential of the aqueous effluent to cause gross inorganic pollution in receiving surface water bodies (Osibanjo, 1992). This could lead to reduction in population of aquatic organisms. The conductivity value of 5.320 µs/cm is very high, which suggest that the sludge contain high concentration of ions. Ogbeibu and Victor (1995) described conductivity as an index of total ionic content of a water body. The high concentration of ion in the sludge suggests that they can be removed by coagulation and flocculation (Asia*, et al*., 2006).

DPR has no limits for nitrate, sulphate and phosphate ions. The result obtained for phosphate is low with 0.98mg/l. However, the presence of these inorganic nutrients (NO$_3^-$, SO_4^{2-} and PO_4^{3-}) in the petroleum sludge could promote plant algae growth if disposed into the environment untreated. The concentration necessary to trigger algae bloom are not well established, but concentration as low as 0.01/mg/l for phosphorus and 0.1mg/l for nitrate may be sufficient for eutrophication when other elements are in the excess (Schindler, 2006). In addition to species diversity and detrimental effect on fresh water and lakes, algae can be toxic to aquatic organisms and affect the taste of water (Morris, 1999).

Analysis of heavy metal content of the petroleum sludge revealed that iron recorded a high value of 494.22mg/l which is extremely above the DPR limits of 1.00mg/l. The high values of iron are in support of earlier studies which showed high iron contents in petroleum sludge (Asia *et al*., 2006; Atuanyan and Tudararo-Ahebrobo, 2015).

The values of zinc 3.791mg/l and copper 3.329mg/l) were higher than the DPR limits of 1.5mg/l and 1.00mg/l respectively, while the values of nickel and lead were 4.537 and 2.590mg/l respectively being above the DPR limits of 0.05mg/l. The only heavy metal that showed a low value was vanadium with 0.910mg/l. The high concentrations of these metal cations have been shown to inhibit microbial activities by causing damage or inactivating one or more critical enzymes which may result in formation of an inactive complex between the metal cations and an active enzyme (Wang and Bartha, 1990).

The high values of TPH (38, 993.2mg/l) and THC (915.0mg/l) contained in the petroleum sludge studied is considered to have contaminating effects on human health and the environment. TPH contain toxic compounds such as polyaromatic hydrocarbons (PAHs) which have also been implicated in inhibition of microbial activities (Dokaniakis, et. al; 2005).

In conclusion, the findings from this study revealed that the petroleum sludge sample from oil processing industry has high pollution potentials and therefore must of necessity be properly treated by ecofriendly methods before disposal to any receiving environment to avoid serious hazardous effects to aquatic and terrestrial organisms as well as man.

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