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Full Length Research Paper

Characterization and treatment of sludge from the petroleum industry

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Samples of sludge from the petroleum industry were collected and characterized for their pollution characteristics. The solids concentration, pH, temperature, biochemical oxygen demand, chemical oxygen demand, dissolved oxygen, phosphate, nitrogen, conductivity, calcium, magnesium, sodium, potassium, iron, manganese, lead and chromium were determined. The analysis revealed that the mean value of total solids (TS) content, total suspended solids (TSS) and total volatile solids (TVS) were 1987, 1050 and 937 mg/l respectively. The dissolved oxygen (DO) content was 3.7 mg/l. The biological oxygen demand (BOD) and chemical oxygen demand (COD) were 518 and 1345 mg/l, respectively. The total nitrogen and phosphorus contents were 3.4 and 2.3 mg/l respectively. The total bacteria counts were 7.4 x 10^8/100 ml. All these values exceed those of the standard as set by World Health Organisation (WHO) for potable water. This shows that the sludge has high pollution potentials and so need treatment before disposal. The COD:BOD ratio was 2.60 which indicated that the sludge can undergo biodegradation and suggests that biological method could be used in effecting treatment to the sludge. The high conductivity also indicated that the sludge can be treated by physicochemical method of coagulation and flocculation.

Key words: Petroleum sludge, pollution characteristics, eutrophication, biodegradation, aerobic treatment,physicochemical method.

INTRODUCTION

The degradation of the environment due to discharge of polluting sludge from industrial sources is a real problem in several countries. This situation is even worse in developing countries like Nigeria where little or no treatment is carried out before disposals. As steps are taken to maintain and improve the quality of surface waters, the quantities of sludge generated by these industries continue to increase, and municipalities and industries are confronted with an urgent need to develop safe and feasible alternative practices for sludge management.

The nature of industrial sludge depends on the source of the wastewater. It could contain not only organic and inorganic matter, but also bacteria and viruses, oil and grease, nutrients such as nitrogen and phosphorus, heavy metals and organochlorine compounds (Priestly, 1991; Bilton, 1994; Lin and Hsiu, 1997). Each component of the sludge has its own environmental impact.

It is a general knowledge that the activities of oil producing companies affect the environment and the health of the people living within the immediate vicinity of the crude oil processing plant. The attendant hazards may trigger processes that may have adverse effects on the ecosystem of such areas. Water used (wastewater) during extraction of crude oil are contaminated and may contain varying quantities of organic matter, heavy metals, volatile hydrocarbons (such as benzene, xylene, and toluene) and many other potentially toxic compounds (Reed and Johnsen, 1995). This wastewater contains sludge, which are disposed off in an environmentally unfriendly manner.

Sludge disposal is a worldwide problem and a wide variety of disposal routes have been adopted as dictated

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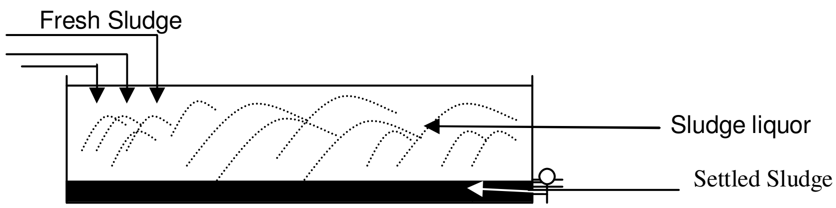

Figure 1. Schematic diagram of sludge sedimentation.

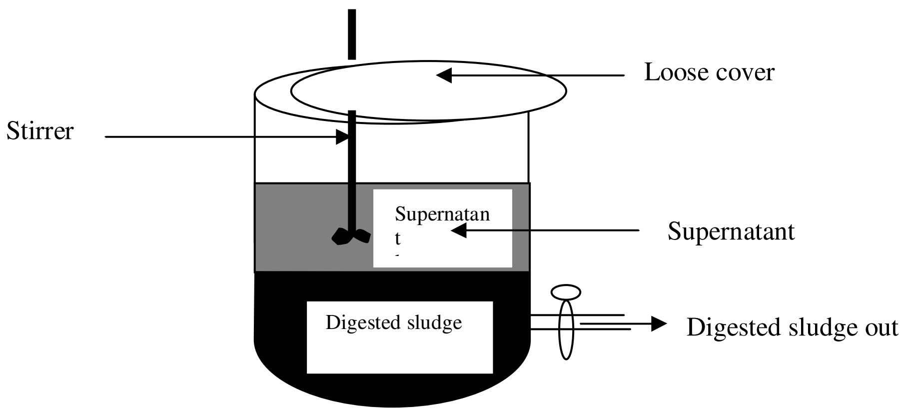

Figure 2. Laboratory apparatus for conducting aerobic digestion studies.

by local conditions. Because of the dramatic increase in the volumes of wastewater treated, large volumes of sludge need to be disposed off in an environmentally safe manner. There is therefore the need to effect proper treatment to sludges before disposal or reuse.

This study attempted to characterize wastewater sludge from the crude oil processing plant located within the Utorogu Community in Ughelli North Local Government of Delta State., and compares the values obtained for the respective pollutants with the Department of Petroleum Resources (DPR) Limits (DPR, 1991) and World Health Organisation Standards (WHO, 1971) for portable water in order to assess the general level of pollution of the wastewater.

MATERIALS AND METHODS

Industrial sludges

The sludge used was obtained from the discharged pit of a petroleum-processing factory located at Utorogu Community in Ughelli North Local Government Area of Delta State. It houses a gas plant station. The gas plants process natural gas and associated crude oil for domestic consumption and export.

Sampling techniques

Sludge samples were collected at the discharge pit of the station. Samples were collected from about 7 different spots within the flow line of the wastewater in the discharge pit and mixed together to form a composite sample. A total of 49 samples (weekly sampling) were collected for analysis. Samples were collected separately for some parameters so as to preserve the composition. pH, temperature, and dissolved oxygen (DO) were determined *in situ* on the field.

The day for sample collection in the new week was different from that of the preceding week. This was done so that the total exercise might account for the cyclic and intermittent variations occurring at the work site.

Samples were collected from the industry once a week for seven weeks and analysed. Where analysis could not be carried out immediately, samples were preserved in a refrigerator maintained at 4ºC. At this temperature, Microorganisms in the sludge are inactivated to prevent biodegradation.

Sample preparation

Sludge was sampled as described under sampling. Four litres of the sludge was put into a plastic container as illustrated in the diagram in Figure 1. The sludge was allowed to sediment for 1 h in order to separate the liquor from the settled sludge. The sludge liquor was used for analysis for the following parameters: pH, temperature, conductivity, specific gravity, turbidity, dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), total alkalinity, hydrogen carbonate alkalinity, ammonia nitrogen, nitrate nitrogen, chloride, sulphate, and total bacteria count.

Settled sludge samples were used for suspended solids, volatile solids, total solids, ash, total nitrogen, phosphorus, potassium, oil and grease, iron, calcium, magnesium, manganese, copper, cadmium, chromium, lead and zinc.

Table 1. Characteristics of fresh sludge liquor from petroleum processing industry.

Sludge liquor characteristics	Unit	Range of values	Mean
pH	-	5.21 – 7.40	6.70
Temperature	ºC	29.5 – 38.5	36.0
Conductivity	Scm^{-1}	19 – 35.5	120
Specific gravity	-	1.03 – 1.12	1.05
Turbidity	NTU	740 – 1145	980
DO	mg/l	2.9 – 3.8	3.7
BOD_5	mg/l	410 – 580	518
COD	mg/l	1015 – 1440	1345
Total alkalinity	mg/l	90 – 150	130
Hydrogen carbonate alkalinity	mg/l	38.4 – 45.3	42
Ammonia nitrogen	mg/l	1.11 – 1.9	1.5
Nitrate nitrogen	mg/l	0.83 – 2.1	1.8
Chloride	mg/l	127 – 159	134.2
Sulphate	mg/l	12 – 19.6	17.2
Total bacterial count.	/100 ml	$(3.1 – 4.1) \times 10^9$	7.4×10^8

Methods of analysis

All samples were analyzed as described in the Standard Methods for the Examination of Water and Wastewater (APHA, 1985) and sandard methods for water and effluents analysis (Ademoroti, 1996). Where analysis was not immediately possible, they were preserved to inhibit biodegradation. All the reagents used for the analysis were of analytical grade and obtained from BDH Chemicals Limited Poole England.

Two litres of sludge was placed in a 4 litre plastic container which serves as the digester (Figure 2). Natural air serves as the aeration system. 5 ml of phosphate solution were added as buffer, 1 ml each of magnesium sulphate, calcium chloride, and iron (III) chloride solutions were added as nutrient for the bacteria population in the sludge. 1\ml of 50% hydrogen peroxide was also added so as to keep dissolved sulphide below 0.6\mg/l and eliminate odour. The plastic container was covered with loose plastic cap to allow air to enter. The sludge was stirred at an interval of 6 h and was allowed to digest for 45 days (Asia, 2000). After this period digestion was deemed to have been completed because of the steady pH obtained. The sludges were thereafter analysed to determined compositional changes and then treated with bleaching powder (calcium oxochloride) until residual chlorine was between 0.2 and 0.7 mg/l (Henry and Heinke, 1989). This was to ensure maximum level of bacteria kill before dewatering. Dewatering was by sand bed filtration using Teflon as the filter medium. The wet sludge was pasteurized for 30 min at 100ºC and sun dried for three days.

RESULTS AND DISCUSSION

The results of the characterization carried out on fresh sludges obtained from a petroleum industry are presented in Tables 1 and 2 while Table 3 contains the Department of Petroleum Resources (DPR) Limits for some of the parameters in Tables 1 and 2. From the results, the pH value for fresh petroleum sludge is 5.48. This indicates that fresh petroleum sludge is acidic. Studies had shown that low pH is toxic to fish and other aquatic lives (Baker and Schofield, 1982).

The temperature values fell within the DPR Limits. Turbidity values for the station were higher than the DPR Limits. The turbidities of 980 NTU showed that the colloidal matter in the sludge was high and by implication the sludge contained high solids concentration. The total solids, suspended solids and the volatile solids were 1987, 1050 and 937 mg/kg, respectively. The BOD, COD and the total bacteria count of fresh sludge were 518 mg/l, 1345 mg/l and 7.4×10^8/100 ml, respectively. These values are quite high when compared to DPR Limits and WHO standard. The dissolved oxygen (DO) of 3.7 is quite low. These indicate strong pollution potentials and therefore call for treatment before disposal. The high COD values and low DO values indicate the high potential of the aqueous effluents to cause gross inorganic and organic pollution in receiving surface water bodies (Osibanjo, 1992). This could cause a reduction in the population of fishes, other aquatic organism, and algae “boom” in surface water bodies, a condition known as eutrophication of water bodies.

The result also shows that the ratio of COD: BOD was 2.60. This indicates that the sludge is capable of undergoing about 50 to 90% substrate biodegradation (Quano et al., 1978) and therefore amenable to biological methods of sludge treatment. On the other hand, Conductivity values of 120 s cm^{-1} are generally high and suggest that the sludge contain high concentration of ions which can be removed by coagulation and flocculation. Oil and grease values of 50.8 mg/kg were high when compared to DPR limits of 10 mg/l. The total alkalinity values were appreciably low. Salinity values of 83.03 mg/l were low when compared to DPR limits.

Department of Petroleum Resource has no Limits for SO_4^{2-}, NO_3^-, and NH_4^+ ions. However, the results obtained for SO_4^{2-} is lower than WHO standard. As could be observed from the results, 1.5 mg/l for NH_4^+ were

Table 2. Characteristics of fresh settled sludge from petroleum processing industry.

Sludge liquor characteristics	Unit	Range of values	Mean
Total suspended solids	mg/kg	840 – 1580	1050
Total volatile solids	mg/kg	819 – 1201	937
Total solids	%	1090 – 2439	1987
Ash	mg/kg	19.5 – 24.7	23.0
Total nitrogen	mg/kg	1.44 – 7.9	3.4
Phosphorous	mg/kg	1.1 – 4.9	2.3
Potassium	mg/kg	1.80 – 2.2	2.03
Oil and grease	mg/kg	320 – 670	508
Salinity	mg/kg	35.4 – 102.5	83.6
Total Iron	mg/kg	3.11 – 12.17	10.13
Calcium	mg/kg	50.1 - 80.4	68.1
Magnesium	mg/kg	35.7 - 56.6	47.5
Manganese	mg/kg	Nil	Nil
Copper	mg/kg	0.26 – 0.52	0.36
Cadmium	mg/kg	Nil	Nil
Chromium	mg/kg	0.01 – 1.05	0.46
Lead	mg/kg	0.08 – 1.45	0.92
Zinc	mg/kg	1.04 – 1.61	1.42

Table 3. Available Department of Petroleum Resources (DPR) limits (DPR, 1991) for some parameters.

Parameters	DPR Limits
pH Max.	8.5
Min.	6.5
Temperature	35 °C
Turbidity	10.00 NTU
TSS	50.00 mg/l
Salinity	600.00 mg/l
Oil & Grease	10.00 mg/l
COD	40.00 mg/L
BOD_5	10.00 mg/l
Cr^{6+}	0.03 mg/l
Total Fe	1.00 mg/l
Cu^{2+}	1.00 mmg/l
Zn^{2+}	1.50 mg/l
Pb^{2+}	0.05 mg/l

higher than the standard of 0.5 mg/l set by WHO for portable water. Consequently, if these sludges containing high concentrations of ammonium are discharged to the environment, depletion of receiving water oxygen resources may occur due to oxidation of ammonia to nitrate by some group of aerobic bacteria. According to Hackman (1978) excess nitrate causes irritation to the gastro intestinal tract, causing diarrhea and dieresis. Methaemoglobinemia, a condition characterized by cyanosis and which can result in infant and animal death can be caused by high nitrate concentration in waters when used to prepare baby foods. Also, nitrate and phosphates, derived from sludges are inorganic nutrients, which promote plant and algae growth. The amount necessary to trigger algae blooms are not well established but concentrations as low as 0.01 mg/1 for phosphorus and 0.1 mg/1 for nitrate may be sufficient for eutrophication when other elements are in excess (Henry and Heinke, 1989). In addition to having a detrimental aesthetic effect on lakes (odour and appearance), algae can be toxic to cattle, spoil the taste of the water, plug filtration units and increases chemical requirements in water treatment (Henry and Heinke, 1989).

The values for total iron were above the DPR Limits with a range of 3.11 to 12.17 mg/l. Chromium values of 0.46 mg/kg for the sampled station were also above the DPR limits, 0.03 mg/l. The high values of iron possibly had given support to earlier studies, which showed that Nigerian soils contain high iron content (Mombeshora et al., 1981). It has been suggested that the operative chemicals used in the treatment of crude oil could be an additional source of iron in the water bodies. Also, since chromium chief ore occurs as iron (II) tetraoxochromate (III) ($FeCr_2O_4$), this might have in part raised the overall level of chromium in the crude and hence, the possible high value of chromium recorded in the sludge.

Lead values were relatively higher than the DPR limits with a range value of 0.08 to 1.5 mg/kg. The high value of lead could be attributed to the use of Pb additives in gasoline marketed in Nigeria. The lead level in Nigeria's gasoline is between 600 and 800 mg Pb per litre which is higher than the permissible levels of Pb in gasoline in the

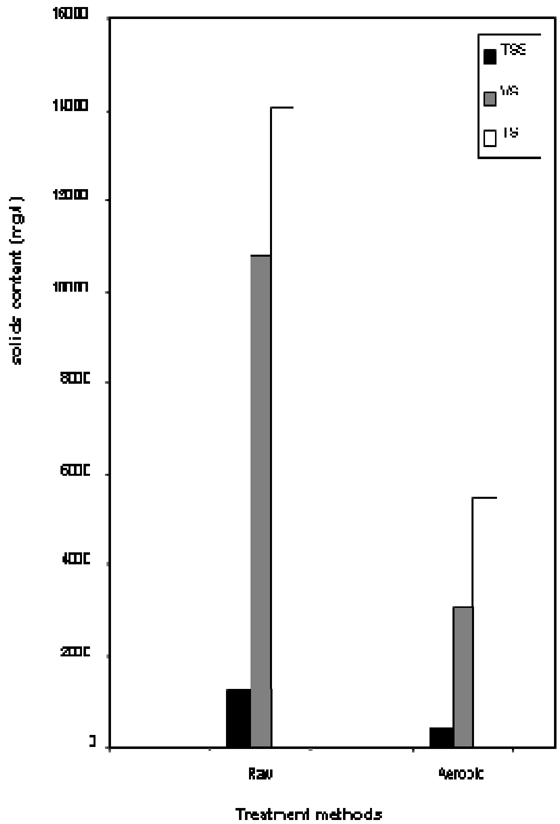

Figure 3. Results of solids content of raw and treated sludge.

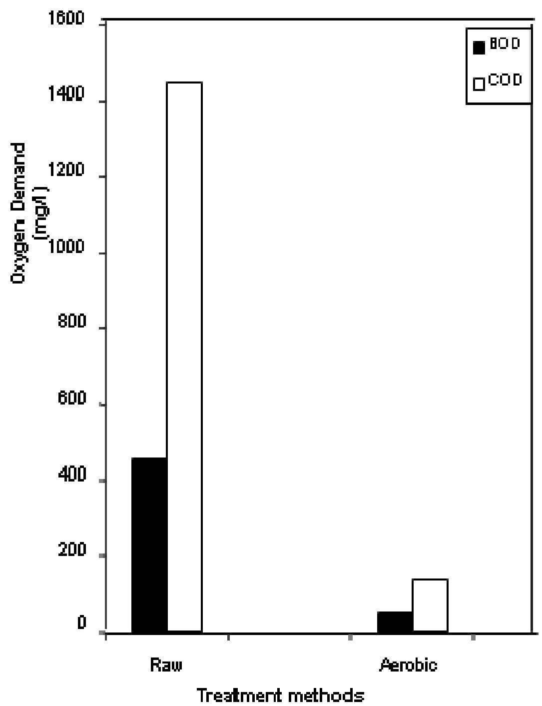

Figure 4. Results of BOD and COD of raw and treated sludge.

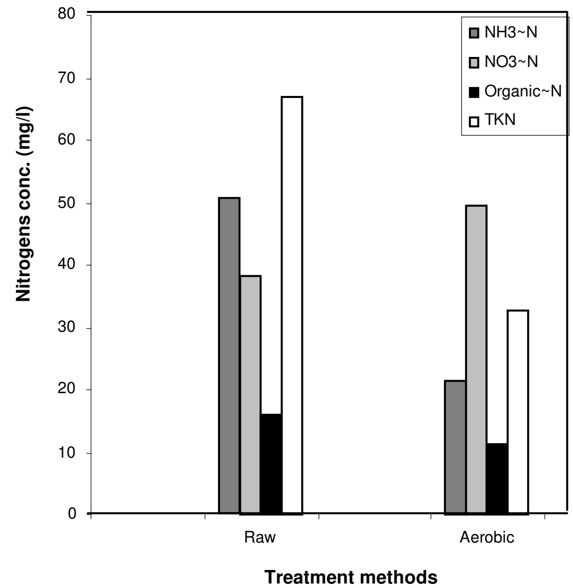

Figure 5. Results of Nitrogens concentration of raw and treated sludge.

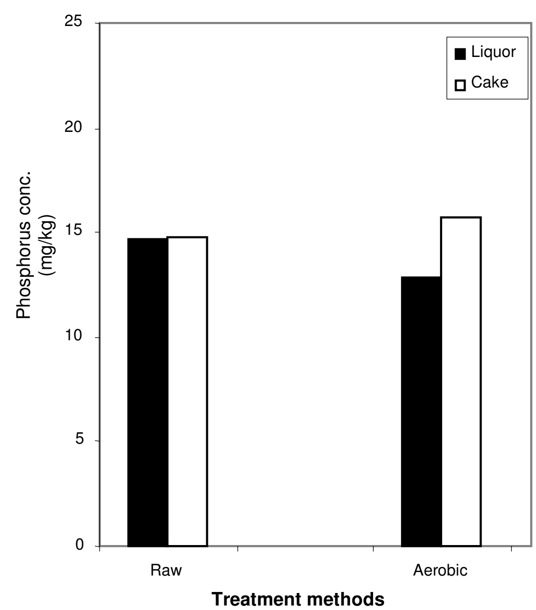

Figure 6. Results of phosphorus concentration of raw and treated sludge

UK and USA (Kakulu and Osibanjo, 1992). The results obtained for copper and zinc showed a strong compliance with the DPR Limits for the sampled station. Figure 3 depicts the results of the amount of solids present in the raw and treated sludge. From the results, it was found that petroleum sludge treated by aerobic method had solids reductions of 24.7 to 28.8% total solids, 25.1 to 34% suspended solids and 38 to 42% volatile solids. The results of the oxygen-demand concentrations of raw and treated sludge shown in Figures 4 reveals that the treatment method proved efficient in terms of BOD and COD reduction. About 94.6 to 96.2% BOD and 95.8 to 97.5% COD reductions were achieved by the treatment method.

Results of nitrogen concentrations in the sludge depicted in Figure 5 shows that there were considerable reductions in the nitrogen content of treated sludge. Ammonia nitrogen reductions in this sludge were in the range of 82.2 - 90.3%. This may be due to the nitrification process during the digestion stage in which some of the ammonia present was converted to nitrate. The result of phosphorus concentrations as shown in Figure 6 reveals that the treating method could be used to reduce phosphorus from the sludge liquor. This phosphorus is adsorbed by the sludge solids, thereby rendering the liquor free from this agent of eutrophication.

In conclusion, the present study revealed that sludge from petroleum processing industry has high pollution potentials and that aerobic biological method is an efficient method of its treatment. The choice of aerobic method over anaerobic system lies in the fact that petroleum industry produces a large volume of sludge coupled with a high concentration of BOD and COD and volatile solids. Keeping economy, time and efficiency in view, an aerobic treatment system is recommended for petroleum sludge. This is due to the presence of aerobic organisms with a high respiratory rate, which acclimatizes and treats the sludge in a short period of time.

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