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CHEMICAL OXYGEN DEMAND (COD) AND BIOCHEMICAL OXYGEN DEMAND (BOD) VALUES OF SOME PETROCHEMICALS

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ABSTRACT

A total of 41 unused petroleum based products classified into four groups were analysed to determine the extent of biological oxidation before their introduction into the environment. They comprised of solvents (18), fuels (6), lubricants (11) and miscellaneous products (6). The chemical oxygen demand (COD) values ranged from 0.6 ? 0.01 to 1.68 ? 0.36g/g for solvent, 0.16 ? 0.07 to 0.4 ? 0.04 for fuels; 0.15 ? 0.003 to 0.82 ? 0.03 for lubricants and 0.02 ? 0.01 to 1.7 ? 0.01 for miscellaneous products. The BOD values obtained were between 0.42 x 10^{-3} and 47.28 x 10^{-3} for fuels; 0.08 x 10^{-3} and 4.80 x 10^{-3} for lubricants; as well as 0.09 x 10^{-3} and 11.10 x 10^{-3} g/g of O_2. For these products the COD/BOD rates ranged from 0.03 to 3.30%. These values have considerable implications for the environment.

INTRODUCTION

Since the advent of the modern petrochemical industry, petroleum has been processed to yield products meant for specialised purposes. The term petrochemical has come to mean all chemical products derived from petroleum fraction and bye-products or those from natural gas constituents (**Albert, 1970**). Petrochemicals fall into different groups including crude oil, fuel, lubricant and hydraulic fluid, solvents, agricultural oil as well as miscellaneous products. These products have different composition from the original fraction initially produced after refining. These petrochemicals are often sources of environmental pollution arising from accidental leakage or spill and leading to widespread contamination and ecosystem disruption. In the two decades spanning 1976 – 1997 a total of 5,334 cases of crude oil spillages have been decade reported in Nigeria releasing 2.8 million barrels of oil into the land, swamp, estuaries and coastal waters (**Odiete, 1999**). When these petrochemicals are released into the environment, they are degraded into simple compounds by physico-chemical or biological agents, with or without human assistance. In the mean time they cause damage to the biota or their physical surrounding. This has been a sore point leading to unprecedented agitation and environmental activism in the Niger Delta region. The pollution extent (concentration) of these chemicals can be measured by analyses such as biochemical oxygen demand (BOD) and chemical oxygen demand (COD). A combination of these two measurements yields information about the biodegradability of the spillage. It is therefore important for all parties concerned with petrochemical production processes, environmental conservation and petrochemical utilisation to known how the components respond to BOD and COD testing, hence, how long spills will last in the environment. This underlies the reason for the present study with a view to determining the COD and BOD of fuels, lubricants and miscellaneous products produced in our refineries in Nigeria

EXPERIMENTALS

Collection of samples: Samples of the petrochemicals used in this study were procured from petrol dealers, vehicle spare part merchants and auto-mechanics in Ibadan metropolis, Nigeria.

Preparation of reagents: For the determination of COD the following reagents were prepared in the laboratory:

1. Potassium dichromate N/8
2. Ferrous Sulphate N/8
3. Saturated Silver Sulphate
4. 1,10 phenatholine indicator.

For the biological oxygen demand (BOD): Manganous sulphate solution, iodide solution, potassium iodate N/40, sodium thiosulphate pentahydrate, starch indicator and ferric chloride solution were prepared. Also for this purpose calcium chloride, magnesium sulphate and phosphate buffer solutions were prepared.

Standardisation of ferrous sulphate for COD: Prior to the determination of the COD in the samples, potassium dichromate was used to standardize the ferrous sulphate for this a known volume of $K_2cr_20_7$ was pipetted into a conical flask. Then 10 ml of sulphuric acid ($H_2 So_4$) and 45ml of distilled water were added. This mixture was then tritrated with N/8 ferrous sulphate to reddish brown using 1,10 phenathroline indicator.
Determination of COD: Prior to the determination of the COD of sample the COD of potassium hydrogen phthalate (KHP) was determined in order to evaluate the procedure of choice.

For the standard and the sample 5ml and 0.06g of the standard and the sample was taken respectively. A known volume of potassium dichromate was added to the sample and KHP. 10 ml of concentrated sulphuric acid 18.1m was added to the content of the round bottom flask. The content of the flask was cooled in a tray containing cold running water, 1ml of silver sulphate catalyst was added to the resulting solution in the flask and refluxed for 2 hours. Distilled water (45ml) was run down through the condenser into the content of the flask. The flask was then cooled in running water. The cooled solution was titrated against ferrous sulphate solution using 1,10 phenatholine indicator until a reddish brown colour appeared.

Determination of Biochemical Oxygen Demand (BOD). Dilution water was first prepared. For this 40 litres of clean tap water was aerated for 24 hours by passing compressed air into it. Phospahte buffer, magnesium sulphate, calcium chloride and ferric chloride (1ml each) were added per litre of water. The water was then seeded by adding 5ml sewage per litre of water and the whole content was thoroughly mixed.

Two sets of BOD bottles of the same size were used for the analysis. A constant percentage (by volume) of the sample was added to the bottle in two sets and it was filled up by the dilution water already prepared. The dissolved oxygen was determined immediately by Winkler's method. This gave D_1 The second set was kept in the dark to incubate for 5 days and the dissolved oxygen determined by Winklers method to give D_5. Two sets of blanks were made by filling two BOD bottles of equal size with the dilution water only and their dissolved oxygen (Do) were determined before and after 5 days incubation. The BOD_5 was calculated as follows:

$$BOD_5 \text{ mg/l} = \frac{(D_1 - D_5) - (B_1 - B_5)}{P}$$

Where

D_1 = Do before incubation
D_5 = Do after 5 days incubation
B_1 = Do of dilution water before incubation
B_5 = Do of dilution water after 5 days
F = Percentage seed in d1
Percentage seed in B,
i.e ratio of seed in sample to see din control
P = Decimal fraction of sample
$= \frac{\text{Volume of sample used}}{\text{Total volume of bottle.}}$

RESULTS

The COD, BOD and BOD_5/COD ratios of five groups of petrochemicals have been determined in the present study. Namely, these are solvents, fuels, lubricants and miscellaneous products.

Solvents: The COD and BOD values of solvents were generally low. They ranged from 0.06 ? 0.01 to 1.68 ? 0.36 for COD and the BOD_5 ranged from 0.08×10^{-3} to 1.73×10^{-3}. These low values indicate the low degradability of the solvent components of Nigerian petrochemicals. The highest BOD_5/COD ratio (%) was 1.97 (2,2,4,4 tetramethyl paraffin). This is also considered low. It showed that the ability of sewage microbes to oxidize the solvents is very low.

Table 1: COD, BOD_5 and BOD_5, COD Values of solvents in petrochemicals

Solvent	Mean ? SD COD g/g/	BPD_5g/g x 10^{-3}	BOD_5/COD (%)	Density g / cm^3
Phenol	1.68 ? 0.36	0.52	0.03	0.96
Butanol	0.56 ? 0.19	6.86	1.23	0.82
Benzene	0.47 ? 0.01	0.28	0.06	0.88
Toluene	0.22 ? 0.01	0.53	0.24	0.90
2, 2, 4, 4, tetramethy paraffin	0.06 ? 0.01	1.18	1.97	0.73
Paraffin oil	0.190 ? 0.004	0.16	0.08	1.23
Acetic anhydride	0.14 ? 0.02	1.73	1.23	1.10
Propanoic acid	0.290 ? 0.004	0.08	0.03	1.99
Ethyl Acetate	0.330 ? 0.002	2.10	0.64	1.10
CCL_4	0.06 ? 0.01	0.08	0.13	1.16
Trimethyamine	0.55 ? 0.01	1.10	0.20	0.74
1, 4 Dioxan	0.640 ? 0.004	0.23	0.04	1.06
Acetone	0.63 ? 0.02	0.77	0.12	0.84
Petroleum ether	0.21 ? 0.02	0.53	0.25	0.72
Hexane	0.13 ?0.09	0.67	0.52	0.66
Thinner	0.29 ? 0.06	0.60	0.21	0.76
Woodlacquer	0.10 ? 0.01	0.12	0.12	0.89

Fuels: The COD values of the six fuels analyzed in this study ranged from 0.16 ? 0.01 to 0.41 ? 0.04 while those of the BOD_5 were between 0.42 x 10^{-3} and 7.28 x 10^{-3} g/g of O_2. (Table II). These values are low, but the processed oil (kerosene, gasoline and diesel) have lower values of COD and higher values of BOD_5 than the crude oil (Forcados, Bonny medium and Bonny light).

Table II COD, BOD_5 and BOD_5/COD values of fuels in petrochemicals

Fuel	COD g/g/	BODx10^{-3}g / g	BOD_5/COD (%)	Density g / cm
Kerosine	0.16 ? 0.07	0.50	0.31	0.80
Gasoline	0.22 0 ? 0.004	7.28	3.30	0.73
Diesel	0.31 ? 0.01	0.51	0.16	0.86
Forcados	0.41 ? 0.04	0.54	0.13	0.89
Crude oil Bonny medium	0.40 ? 0.01	0.48	0.12	0.87
Crude oil Bonny light	0.280 ? 004	0.42	0.15	0.88

Table III: COD, BOD_5 and BOD_5/COD values of lubricants in petrochemicals.

Lubricant	COD g/g/	BOD_5g/g x 10^{-3}	BOD_5/COD (%)	Density g / cm^{-3}
Engine oil (SAE 40)	0.27? 0.01	0.08	0.03	0.90
Engine oil (SAE20 – 50)	0.180 ? 0.004	0.47	0.26	0.71
Gear oil	0.33 ? 0.01	1.96	0.59	0.93
Brake oil	0.820 ? 0.003	2.42	0.29	1.03
Lubricating oil	0.31 ? 0.01	0.50	0.16	0.85
Penetrating oil	0.26 ? 0.003	4.80	0.18	0.87
Shock absorber	0.19 ? 0.01	0.50	0.26	0.87
Ruba S40 (TOTAL)	0.20 ? 0.01	0.35	0.18	0.92
Oil treatment (Redex)	0.150 ? 0.003	0.65	0.43	0.79
Steering oil	0.33 ? 0.01	4,80	1.40	0.85

Lubricants: The range of values was from 0.150 ? 0.003 to 0.820 ? 0.001 for COD while the BOD_5 ranged from 0.08 x 10^{-3} to 4.80 x 10^{-3}.

Miscellaneous Products: Analyses showed that COD and BOD values also were fairly low. (Table IV). The COD was between 0.02 ? 0.01 (for rust remover) and 1.71 ? 0.01 (petromate). Also the BOD_5 ranged between 0.09 x 10^{-3} (Car Wash Detergent) and 11.10^{-3} x 10^{-3} (petromate).

Table IV: COD, BOD_5 and BOD_5/COD values of miscellaneous petrochemicals in petroleum.

Miscellaneous	COD g/g	BOD_5g/g x 10^{-3}	BOD_5/COD (%)	Density g / cm^3
Rust remover	0.02 ? 0.01	0.16	0.80	1.16
Antirust	0.04 ? 0.01	0.15	0.38	1.57
Varnish	0.14 ?0.01	0.37	0.26	1.28
Car was (detergent)	0.22 ? 0.01	0.09	0.04	1.06
Radiator coolant	0.14 ? 0.01	0.12	0.09	0.99
Petromate	1.71 ? 0.01	11.10	0.65	0.78

DISCUSSION

The values of the BOD_5, COD and their ratio which expresses the extent of biological oxidation of four groups of petrochemicals namely solvent, fuel, lubricant and miscellaneous chemicals, have been determined in the present study. The BOD values show that propanoic acid and tetra-chloro ethane (solvents) as well as engine oil (lubricant) had the lowest values of 0.08 x 10^{-3} g/g of O_2 while petromate (miscellaneous product) had the highest value of 11.1 x 10^{-3} g/g of O_2. Also, the COD gave values of between 0.02 to 1.71 g/g of O_2. The least oxidised material was the antirust. These results indicate that microbial activities on the hydrocarbons were very low. The low consumption of oxygen may be due to the low level of micro-organism (hence their actively) in sewage effluent used for seeding the dilution water.

The BOD_5/COD ratio represents the extent of oxidation of petrochemical by sewage micro-organism. The ratio obtained indicated that about 0.02 to 3.3 per cent of the petrochemical samples were oxidised by the sewage organism in the 5-day test period. These values were extremely low. Products with BOD_5/COD ratio value of 40% and above are considered to be completely degradable (Gannon et al, 1981). Our values (0.02 – 3.3 g/g of O_2) are far from the limits. This grossly points to the fact that the petrochemicals were largely non-degraded, hence regarded as refractile or contained toxic components.

The results of the present study are at variance with those of Birdie *et al* (1979). The COD, BOD and their ratios by these workers were higher than those obtained in the present study. The variance may be explained in terms of difference(s) in analytical techniques: While Birdie *et al* used allylthiourea to prevent nitrification and prepared seed for their analyses, sewage organisms were used in the present work. Nonetheless, the values obtained were low for the two results. The present work therefore confirms the fact that petroleum–based products were generally poorly oxidised. It is noteworthy that the samples used in this study were previously unused, this further justifies the very low degree of degradation encountered.

Petrochemicals are widely used for domestic and industrial concerns as solvents, fuels, lubricants and so on. This indicates a great interaction with the environment. That our study has shown poor degradability of the petrochemicals used heightens fear that they could have high bio-magnification tendencies. Some of these petrochemicals are known for the toxicity, carcinogenicity and metagenicity occasioned by their poor degradability, the need to design effective means of disposal through recycling and re-use become relevant.

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