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Correlation Studies of Some Parameters in Petroleum Wastewater Obtained From Warri, Delta State, Nigeria

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Abstract— Effluent samples were collected at the discharge pit in the flow line of wastewater stations at one of the petroleum industries in Nigeria. A total of 10 samples were collected for analysis. Physicochemical parameters were analyzed according to Standard Methods for the Examination of Water and Wastewater. The results show that almost all the parameters analysed complied with the Department of Petroleum Resources (DPR) limit for effluent discharge in Nigeria. Mean values obtained for the parameters were within the following range: pH = 5.8 – 6.9, temperature (T) ^{0}C = 30.2 - 33.6, electrical conductivity (E.Cond)µS/cm = 30 – 210.00, dissolved oxygen (DO) mg/L = 4.38 -5.85, total suspended solids (TSS) mg/L = 10.00 - 65.00,total dissolved solids (TDS) mg/L = 15.90 – 121.80,turbidity (Turb) NTU = 5.80 - 45.50,salinity (Sal) mg/L = 6.66 – 53.32, biochemical oxygen demand (BOD)mg/L = 4.72 – 5.89,chemical oxygen demand (COD) mg/L = 7.76 – 8.35. Some parameters of interest were correlated to see the possibility of establishing their relationship. Positive correlations were observed for some parameters pairs like, E.Cond/TDS, Turb/TSS, Turb/TDS, E.Cond/Sal, TDS/Sal, COD/BOD; while negative correlations were observed for parameters pairs like BOD/DO and COD/DO. The effect of these correlations in relation to wastewater monitoring was discussed.

Index Terms— Correlation, regression analysis, Effluent, Petroleum Industries, Physicochemical Parameters,

1 INTRODUCTION

Petroleum industries in Nigeria were established due to immense oil resources discovered in the country. The petroleum resource in Nigeria is located within the coastal Niger delta or south -south region. Overall, petroleum (crude oil and natural gas) accounted for 97% of all government external revenue in Nigeria. The first oil operation began in the 1950's and the political economy of petroleum in Nigeria became characterized by endemic patronage. The petroleum products find a variety of domestic and industrial applications. These products are principally a source of energy and power for industry, transportation and electricity generation. Most of the oil fields are small and scattered all over the country [1].

As one of the few major oil producing nations in Africa, Nigeria's proven reserve of crude oil has been estimated at 280 x 10^9 m^3 (offshore) and 840 x 10^9 m^3 (on shore) . The petroleum reserve in Nigeria is located within the Niger Delta area. The Niger delta is located within latitudes of $5^o 45^1$ and $6^0 35^1$, and longitudes $4^0 50^1$ and $5^0 15^1$ in the central part of southern Nigeria and has a kilometers which accounts for about 8% of Nigeria's land mass.

The Niger Delta comprises 70000 km^2 of wetlands formed primarily by sediment deposition. Home to 20 million people and 40 different ethnic groups, this floodplain makes up 7.5% of Nigeria's total land mass

It is the largest wetland and maintains the third-largest drainage area in Africa. The Delta's environment can be broken down into four ecological zones; coastal barrier islands, mangrove swamp forests, freshwater swamps, and lowland rainforests. This incredibly well-endowed ecosystem, which contains one of the highest concentrations of biodiversity on the planet in addition to supporting the abundant flora and fauna, arable terrain that can sustain a wide variety of crops, economic trees, and more species of freshwater fish, than any ecosystem in West Africa.

Petroleum exploration and production by petroleum industries in Nigeria involve variety of operations and activities. This result in huge waste disposal accompanied with various environmental problems. The bulk of the liquid effluent generated in petroleum industries consist mainly of water and oily wastes [2]. Petroleum exploration and production involves the use of wide range of chemicals in operations especially for well protection and in separation of water from oil. Formation waters and effluents discharges are high essentially in total dissolved solids. Some of the effluent discharges also contain oil sheen and some chemicals injected into the wells to inhibit corrosion of equipment or enhance the separation of oil from water. Such water for example could have harmful effects on plants and animals [3].

Effluents discharged from petroleum industries can vary from time to time depending on the activity being carried out. The effluents can contain organic and inorganic matter, bacteria, viruses, oil and grease. Also nutrients such as nitrogen and

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phosphorus and some heavy metals may be present [4]. The parameters used to characterize industrial effluents are measurable quantities which could be physical, chemical, bacteriological, or a combination of these. In this study, some quality parameters of industrial effluents from a petroleum industry such as pH, temperature, electrical conductivity, dissolved oxygen, total suspended solids, total dissolved solids, turbidity, salinity, biochemical oxygen demand and chemical oxygen demand were determined. Values obtained were used to examine the possible relationship between these parameters.

The aim of the study is to achieve a rapid method of pollution control by accessing the relationship if any, between the parameter pairs; TDS/E.Cond, Turb/TSS, Turb/TDS, E.Cond/Sal, TDS/Sal, BOD/COD, BOD/DO and COD/DO in petroleum effluent. It is believed that in comparing results of the above parameters, useful empirical information may be obtained for estimating one parameter from the other in petroleum effluents. This will facilitate rapid effluent assessment or process control for management decision.

2 Objectives of The Study

The objectives of the study are to:

i. Determine the values of pH, Temp., E.Cond, DO, TSS, TDS, Turb., Sal., BOD, and COD present in some effluent discharges from a petroleum industry.
ii. Attempt to model any relationship that may exist between the parameters pairs: TDS/E.Cond., Turb./TSS, Turb./TDS, Sal./Cond., Sal/TDS using correlation and regression analysis.
iii. Establish if possible, an empirical relationship between the parameters for quick monitoring.

3 Materials and methods

3.1 Sampling

Effluent samples were collected at the discharge pit in the flow line of the wastewater stations. A total of ten (10) samples (5 from each of two facilities) were collected for analysis.
Samples were collected from the locations once a week for six weeks and analysed. Sample period was at 2hours interval for four hours from 10am to 4pm.
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. Where analysis could not be carried out immediately, samples were preserved in an ice cooled pack and maintained at 4^oC. At this temperature, microorganisms in the effluents are inactivated to prevent biodegradation.
The effluent samples were collected from two flow stations and gas plants. Samples were collected in sterilized screw capped polythene gallons of 1 litre capacity, labelled properly and analysed in the laboratory.

3.2 Methods of Analysis

All samples were analysed as described in the standard methods for the examination of water and wastewater [5] and standard methods for water and effluents analysis [6]. All reagents used were of analytical grade and obtained from BDH chemicals. The glass wares used were cleaned by soaking over – night in chromic acid followed by rinsing with tap water and finally in distilled water.
pH, temperature, turbidity, conductivity and salinity of the test samples were determined using Hach water analysis kits (Model DR 2010). Sample measurements were made after caliberation with reference standard from Hach by dipping the cell into the sample. Readings which were displayed on the screen were taken after they had been allowed to stabilize. These determinations were carried out on the spot immediately after collecting the effluent samples.
TSS and TDS were determined gravimetrically. For TSS, each sample was filtered through a Whatman glass fiber filter disc (5.5cm in diameter), using an air pump. Each filter was then placed on a tin tray (the tin trays and glass fiber filter were previously dried at 105^0 C and weighed in the oven) placed in the oven and dried at 105^0C for not less than 2 hours. The trays and used filters were weighed again. The difference between the final weight and initial weight gave the amount of suspended solids in the sample.TSS mg/L was calculated as follows:

mg/L suspended solids= (A-B)×1000/Sample volume used (1)
Where A =Weight of glass fibre filter + dried residue in mg
B = weight of filter paper in mg
Sample volume used = 100mL.

TDS was determined using the filtrate obtained from TSS determination. The filtrate was taken and transferred to an evaporating dish (the evaporating was previously heated in the oven to 180^0C for 1 hr cooled to room temperature in desiccator and weight noted) this was evaporated to dryness on a steam bath. Evaporated sample was dried in the oven for 1hour, cooled in desiccators to balance temperature and weighed. The drying process was repeated until a constant weight was achieved. TDS was calculated as follows:

mg/L Dissolved solids=(A-B)×1000/Sample volume used (2)
Where, A=weight of dried residue = dish in mg
B=weight of dish in mg
Sample volume = 100mL

Dissolved oxygen (DO) was determined using the Azide modification of Winkler's method; Biochemical oxygen demand (BOD_5) was determined by incubating the samples in the dark for 5 days at 20°C. Results were collated as follows:

$$BOD_5 \text{ (mg/L)} = (IDO - DO_5) / P \qquad (3)$$

Where:
IDO = Initial dissolved oxygen in the sample
DO_5 = Dissolved oxygen in the sample after five days of incubation
P = Percent dilution

Chemical oxygen demand (COD) was determined by closed reflux titrimetric method. The well mixed samples were refluxed for 2 hours with standard potassium dichromate digestion solution in the presence of sulphuric acid reagents. After digestion, the excess dichromate was titrated against standard ferrous ammonium sulphate titrant (FAS) using ferroin indicator. Blank determinations were also carried out. The COD was calculated as follows:

$$COD \text{ (mg/L)} = (A-B) \times M \times 8000/\text{mL of sample} \qquad (4)$$

Where:
A = mL of FAS used
B = mL of FAS used for sample
M = Molarity of FAS

4 Results and Discussion

Results obtained from analysis of the effluent samples are presented in this section. Table 1 presents results of effluents characteristics studied while results in Table 2 depicts parameters correlated and results obtained from the correlations. The relationship between the parameter pairs in form of scatter diagrams are as shown in Figures 1 to 8. The analysis carried out to relate one parameter to the other are also discussed.

Table 1. Results of effluents characteristics.

Parameters	*Unit*	*Range of values*	*Mean*	*DPR limit*
pH		5.8-6.9	6.43	6.5 – 8.5
Temperature	^0C	30.2 -33.6	32.00	25
Electrical Conductivity	µS/cm	30 – 210.0	95.2	N/A
Salinity	mg/L	6.66 – 53.32	22.48	600
Turbidity	NTU	5.80 - 45.50	19.99	10
Total Suspended Solids (TSS)	mg/L	10.0 – 65.0	25.3	50
Total Dissolved Solids (TDS)	mg/L	15.90–121.80	55.06	2000
Dissolved Oxygen (DO)	mg/L	4.38 – 5.85	5.12	N/A
Biochemical oxygen demand (BOD)	mg/L	4.72 – 5.89	5.20	10
Chemical oxygen demand (COD)	mg/L	7.76 – 8.35	7.98	10

Table 2: Parameters correlated and results obtained.

S/No	Parameters correlated (y and x axis)	Coefficient of determination (r^2)	Correlation coefficient (r)	Direction of correlation	Regression equation (regression of y axis on x)	Final equation for conversion
1	E. Cond. with TDS	0.999	0.999	Positive	y = 1.716x + 0.683	E.Cond = 1.716TDS + 0.683
2	Turb. with TSS.	0.977	0.988	Positive	y = 0.68x + 2.787	Turb = 0.68TSS + 2.787
3	Turb. with TDS	0.518	0.720	Positive	y = 0.219x + 7.925	Turb = 0.219TDS + 7.925
4	E.Cond. with Sal	0.793	0.891	Positive	y = 3.703x + 11.94	E.Cond = 3.703Sal + 11.94
5	TDS with Sal.	0.794	0.891	Positive	y = 2.158x + 6.538	TDS = 2.158Sal + 6.538
6	BOD with DO	0.587	0.766	Negative	y = -0.588x + 8.216	BOD = -0.588DO + 8.216
7	COD with DO	0.014	0.118	Negative	y = -0.041x + 8.194	COD = -0.041DO + 8.194
8	COD with BOD	0.079	0.281	Positive	y = 0.127x + 7.32	COD = 0.127BOD + 7.32

Results from the effluents analyzed (Table 1) revealed that pH values ranged from 5.8-6.9 with a mean value of 6.43, which showed slight acidity to neutrality. Slight acidity in the effluent may cause harmful effects to aquatic animals when the effluent is eventually discharged to a receiving water body.

For the temperature, ranges of values were from 30.2 – 33.6 with a mean value of 32.00. This was the temperature range for ambient temperature during sampling period. The ranges of values were higher than DPR limit of 25°C but within Federal Ministry of Environment (FME) limit of 35°C for effluent discharge[7], [8].

Values of other parameters obtained were: electrical conductivity (range = 30-210; mean = 95.2) µS/cm, salinity (range = 6.66 – 53.32; mean = 22.48)mg/l turbidity (range = 5.80 – 45.50; mean = 19.99) NTU, TSS (range = 10.0 – 65.0; mean 25.3)mg/L, TDS (range = 15.90 – 121.80; mean = 55.06)mg/L, DO (range = 4.38 – 5.85; mean = 5.12)mg/L, BOD (range = 4.72 – 5.89; mean = 5.20)mg/L and COD (range = 7.76 – 8.35; mean = 7.98)mg/L. These values were also within DPR limit.

4.2 ANALYSIS

An attempt to model the relationship between the parameter pairs was carried out using the linear regression analysis. The coefficient of determination (r^2), correlation coefficient (r), direction of correlation, regression equation and final equation for conversion for the parameter pairs are as shown in Table 2. For correlation to exist, the value r should lie between -1 and +1 (i.e. $r = -1 \leq r \leq +1$). Therefore, r values lie between + 0.01 and + 1.0 for positive correlation and 0.01 and -1.0 for negative correlation [9], [10].

The regression plots of Figures 1 to 5 showed strong positive correlations (r values ranged from 0.720 to 0.999) while plots in Figures 6 and 7 showed negative regression lines. Negative correlation in Figure 6 was strong (r = 0.766) but weak in Figure 7 (r = 0.118). The positive regression lines indicated that in each parameter pair as one parameter was increasing the other parameter was also increasing. The strong positive correlation (r = 0.999) observed between E.Cond / TDS in Figure 1 indicated that inorganic ion concentration was strongly related to the total solid matter in the effluent samples. [11]. Strong, positive correlations were obtained between the parameter pairs: Turb / TSS and Turb / TDS (Figures 2 and 3; r =0.988, r = 0.720 respectively). This showed that turbidity in the effluent was strongly due to the suspended particles or dissolved matter. Therefore colloidal particles such as clay, silt, rock fragments etc which may be present in the aqueous effluent would have influenced turbidity and thus the strength of the relationship [6], [12].

Also, strong and positive correlations were obtained between the pairs: E.Cond / Sal and TDS /Sal in (Figures 4 and 5). Salinity and TDS is usually due to salts of organic and inorganic origin which can also influence conductivity of the effluent samples.

For the negative regression plots between the parameter pairs, BOD / DO; COD / DO (Figures 6 and 7), it showed that as one parameter was increasing, the second parameter was decreasing and vice versa.

Although BOD and DO showed negative regression lines their correlation coefficient of r = 0.766 showed strong correlation (Figure 6). But for the negative regression line in the correlation between COD and DO, the r value of 0.118 showed weak correlation (Figure 7).

The strong but negative correlation observed between BOD and DO revealed the strength between biochemical oxygen demand and dissolved oxygen saturation levels in the effluent. Therefore depletion of dissolved oxygen in the effluent is an indication of high levels of BOD. [13], [14].

Also, the weak but negative correlation observed for COD / DO in Figure 7 revealed that DO saturation level has little or no relationship with the COD levels in the effluent.

However, for the parameters that have negative correlation, the value of one parameter can also be deduced from the other using the regression equation obtained.

The correlation observed for COD/BOD in Figure 8 was also positive but weak (r = 0.281). This was a reflection of the strength of relationship between the biodegradable organics and other substances present in the effluent which could be toxic or non-biodegradable. Such toxic substances may have affected BOD values to a reasonable degree. [15]

However effluent composition and strength will vary from place to place depending on the source or origin. This variation would have taken toll on the values obtained [16].

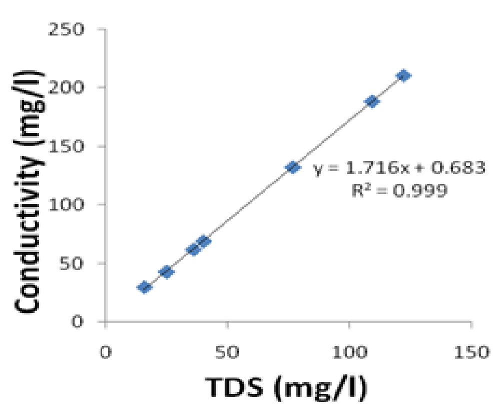


Fig. 1. Correlation of Conductivity with TDS

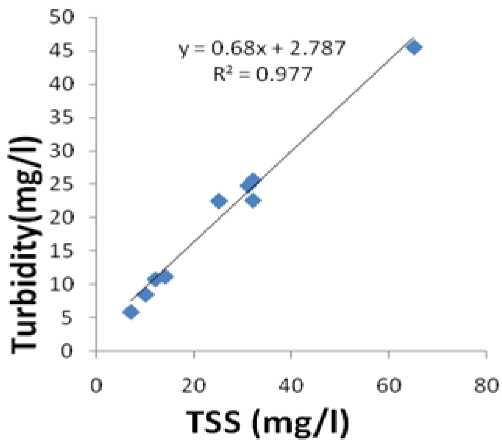


Fig. 2. Correlation of Turbidity with TSS

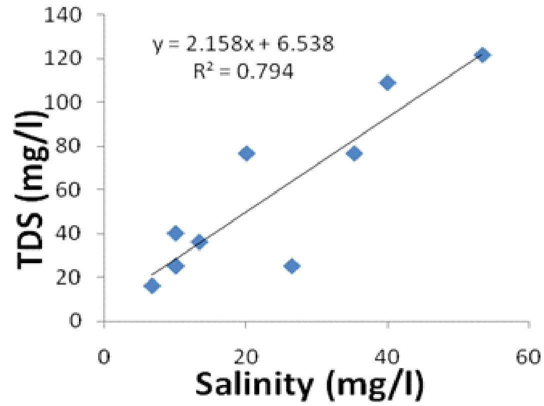


Fig. 5. Correlation of TDS with Salinity

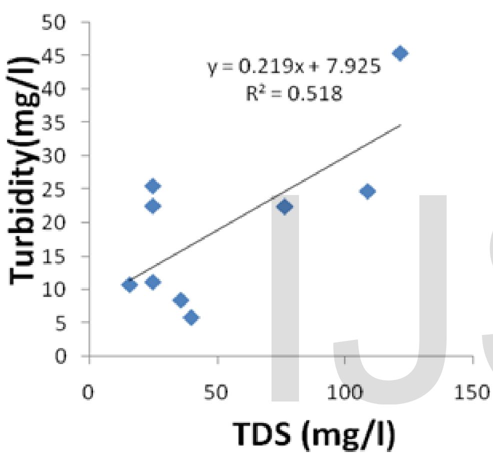


Fig. 3. Correlation of Turbidity with TDS.

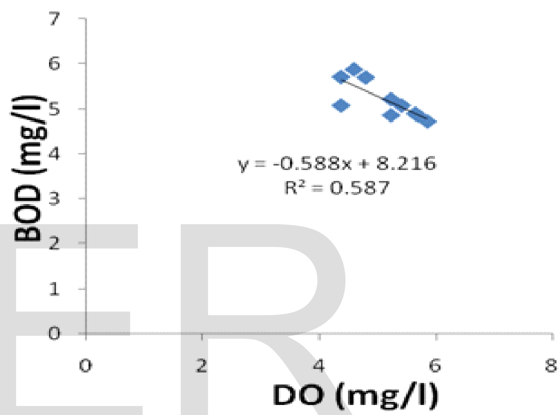
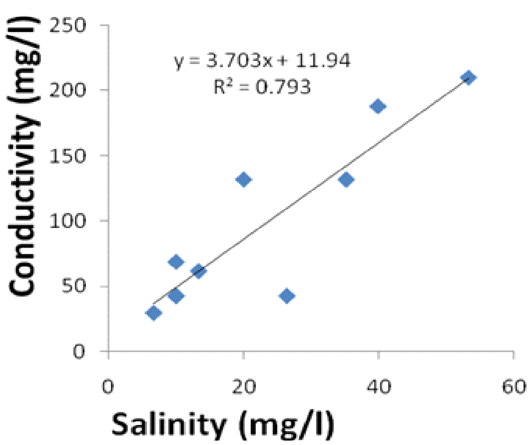


Fig. 6. Correlation of BOD with DO



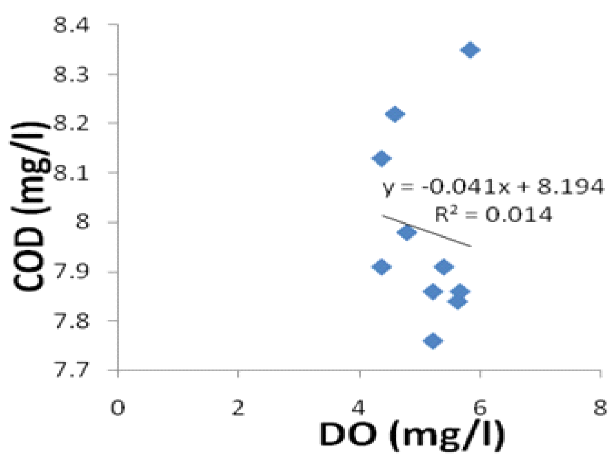


Fig. 7. Correlation of COD with DO

Fig. 4. Correlation of Conductivity with Salinity.

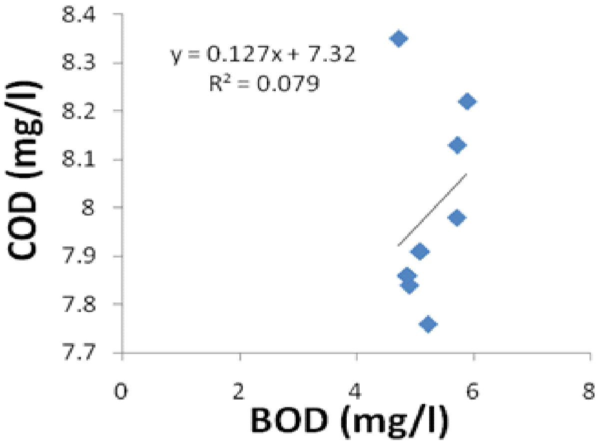


Fig. 8. Correlation of COD with BOD

5 Conclusion

The above analyses and discussions revealed that strong and positive correlation exist between the parameters pairs: E.Cond/TDS, Turb/TSS, Turb/TDS, E,Cond/Sal, and TDS/Sal in the petroleum effluents studied. However, strong but negative correlations exist between the pair: BOD/DO, while weak and negative correlations exist between COD/DO. Also, weak but positive correlation was observed between the parameter pair: COD/BOD. Their correlation coefficients were 0.999, 0.988, 0.720, 0.891, 0.891, 0.766, 0.118 and 0.281 respectively.

Results obtained from the relationships established will serve as useful technique because it will help to save time and reduce cost of monitoring effluent discharges from petroleum industries.

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