

Study on the Variations in Physicochemical Property Concentration in a Contaminated Fresh and Salt Water

OZIOKO F.C.¹, Ekperi, N.I.^{2,*}, OKIRIE Faith Uchendu³

Abstract

In this research, the dispersion of crude oil contaminated was subjected into laboratory observations and results were recorded. These results were used to develop and adopt mathematical models for a proper engineering experimental practice. 1.5m³ volumes of fresh water and salt water were filled in two tanks of equal fit at the same intervals along the tanks and depth, where samples were collected for the purpose of analysis of physicochemical properties or parameters. The TPH diffusion of the experimented contaminated water environment was examined with the used of mathematical equations on dispersion and degradation combined with first order degradation rate and the Monod equation for both salt and fresh water contaminated water environment. This was observed to have gradual increase with time up to day 56. Then, on the day 70 and 80 respectively, a rapid increase was revealed during the experiment. The effect of crude oil was more in the fresh water compared to salt water media. The TPH predicted by the diffusion model incorporated with first order rate kinetics matched closely with experimental data than the model incorporated with Monod equation. The deviation between the predicted TPH by the model incorporated with Monod equation and the experimental data showed Monod Equation may not be suitable to use as rate parameter in the diffusion model. However, either of the models can be used to study the rate of oil sediment in stagnant water media. The experiment revealed that rate of physicochemical parameters in the contaminated water under investigation was high but was drastically reduced after apply a method known as the bioaugmentation technique which helped to accelerate the TPH degradation.

Keywords: Bio-remediation, Stagnant Water, Pollution , TPH , Monod Equation

INTRODUCTION

When crude oil spills cause a wide range of difficulties, it is vital to design a prediction model that will help to degrade and salvage impacted areas. Because of the numerous issues caused by crude oil

spills, it is vital to design a prediction model that will aid in the degradation of the affected region and the removal of the obnoxious threat. In this paper, a predictive model of crude oil degradation and sedimentation in stagnant water media is developed [1, 2]. The influence of dispersion and diffusion of crude oil in stagnant water media is also studied on overall degradation. Consequently, the breakup of the oil and its transport to the water column in addition to the depth of its diffusion are equally the focus of the study [3–5].

With the goal of determining crude oil dispersal and transport on near the coast water over time, [1] created a prediction model for the dispersion of

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three distinct Nigeria crude oil blends in coastal water: Bonny lights, Brass bleed, and Escravos. However, the work did not take into consideration the microbial action on the crude oil degradation as a factor that can cause crude oil concentration gradient [6].

Evaluation of crude oil degradation in fresh water contaminated site was conducted by [7] to determine the Bonny tight crude oil degradation and physicochemical properties of contaminated site with respect to microbial population and time. Indeed, the work did not isolate and identify the bacterial species responsible for the degradation but based the research on microbial population.

[8–9] investigated oxygen scarcity in microcosm models in the bioremediation by varying aeration conditions and comparing results to a set up that approximated oxygen constraint. The research did not consider the sedimentation of the suspended particles as one of the greatest factors affecting the oxygen concentration in the water system.

In a research carried out by [7], on the development of model for crude oil degradation, a mathematical model was used to simulate the rate of degradation of crude oil at an ambient temperature of 18°C–40°C and equally used to correlate specific rate and substrate concentration as a function of distance and time. The research did not include the use of other rate equations other than Monod's equation in the determination of rate of degradation.

The spreading rate force is dependent on the surface tension of the crude and was used to calculate the pace at which oil distributes over the sea floor, according to [9] investigation on the spread of oil spill on a pond aquatic medium. However, the work was limited only to the surface spread of crude oil without taking into consideration the diffusion of the oil down the column of the water body [10].

Research Focus

This thesis on the development of predictive model of crude oil degradation and sedimentation in a stagnant water media was investigated with the aim to outline the objectives as demonstrated below:

- i. To monitor the effect of crude oil degradation on the characteristics of the physicochemical parameters of the environment in line with the role of the functional coefficient as well as the principle of sedimentation.
- ii. To examine by isolation, identification and characterization of the possible microbes capable of degrading the crude oil as well as the microbial count of the various anaerobic and facultative anaerobic organisms present in the stagnant water media.
- iii. Development of mathematical model to predict the rate of crude oil dispersion with respect to depth and time with the action of microbes as contributing factors.

METHODOLOGY

Determination of Nitrate

Determination of nitrate was carried out using ultraviolet spectrophotometric screening method in the course of this research work. The analytic process of addition of 1ml HCl solution into 50 ml filtered sample. Also the calibration standard of the range between 0 to 7 mg NO_3^- N/L by diluting to 550 mL.

Determination of Turbidity

The Samples were diluted with one volume of turbidity-free water until turbidity falls between 30 to 40 NTU and the turbidity was read directly from scale. In order to calculate the original sample's turbidity, the dilution factor and the diluted sample's turbidity were compared. Original Turbidity = Turbidity of Diluted Sample \times Dilution factors. This was calculated as:

$$\text{Nephelometric Turbidity Unit (NTU)} = \frac{A \times (B + C)}{C} \quad (1)$$

Where A = NTU found in diluted sample

B = Volume of dilution water (ml)
 C = Sample volume taken for dilution (ml)

Determination of Alkalinity

The sample was titrated with standard acid solution and the Phenolphthalein end point was obtained and recorded as value (p) for titration to pH 8.3 in ml. The total volume of acid used in the titrating of both indicators was recorded as M.

Where M = Titration to pH 4.5 in ml (Methyl or Orange end point)

P = Titration to pH 8.3 in ml (Phenolphthalein end point). This was calculated as:

$$\text{Bicarbonate (HCO}_3\text{)} \text{ mg/L} = \frac{\text{ML acid} \times \text{N acid} \times 61 \times 1000}{\text{Ml Sample}} \tag{2}$$

$$\text{Carbonate (CO}_3\text{)} \text{ mg/L} = \frac{\text{ML acid} \times \text{N acid} \times 30 \times 1000}{\text{Ml Sample}} \tag{3}$$

$$\text{Hydroxyl (OH)} \text{ mg/L} = \frac{\text{Ml acid} \times \text{N acid} \times 17 \times 1000}{\text{Ml Sample}} \tag{4}$$

Where N = Normality of acid

RESULTS AND DISCUSSION

Pt 1 (0m), pt 2 (0.25m), pt 3 (0.5m), pt 4 (0.75), pt 5 (1m) and pt 6 (1.25).

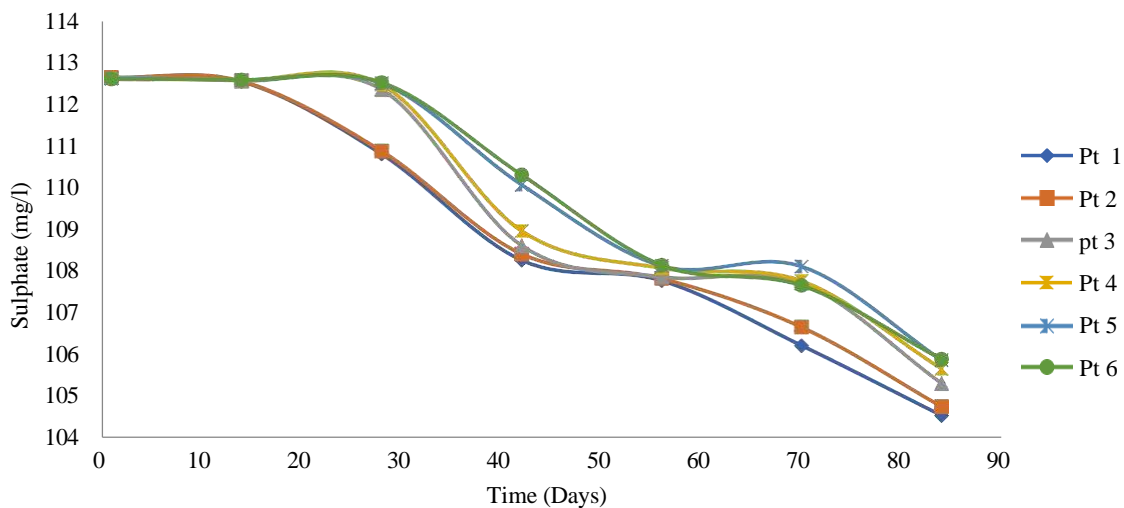


Figure 1. Variation of sulphate in the polluted stagnant fresh water.

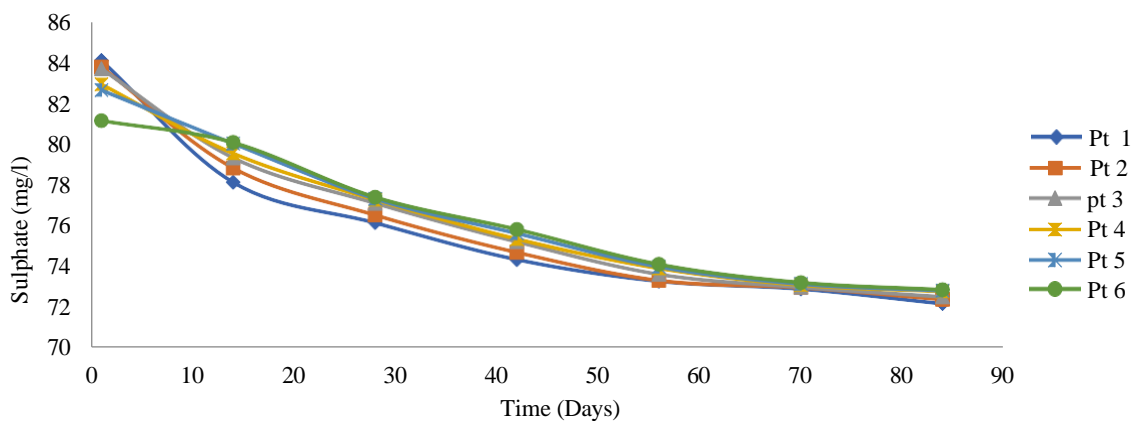


Figure 2. Variation of Sulphate in the Polluted Stagnant Salt Water

Pt 1 (0m), pt 2 (0.25m), pt 3 (0.5m), pt 4 (0.75), pt 5 (1m) and pt 6 (1.25).

Figure 1 illustrate the flow of variation in sulphate in relation to time at different depths. While Figure 2 demonstrates the profiles of sulphate in relation with time for the contaminated salt water environment. Like chloride, sulphate variation in fresh and salt water differs. Initially, the pollution rate influenced by the crude oil into the water samples for the experiment was 38.48mg/l in fresh water and 80.85mg/l in salt water, but after pollution, it increased to 112.64 mg/l in the fresh water and 84.06mg/l in the salt water. Then, the content of Sulphate into salt and fresh water increased in time and varied with increase in depth (Tables 1-4).

Table 1. Sulphate measurement in fresh water.

Time (Days)	Sulphate (mg/l)					
	Pt 1	Pt 2	pt 3	Pt 4	Pt 5	Pt 6
1	112.64	112.64	112.64	112.62	112.62	112.6
14	112.54	112.55	112.56	112.58	112.58	112.58
28	110.8	110.87	112.35	112.47	112.5	112.52
42	108.25	108.4	108.6	108.95	110.06	110.3
56	107.76	107.81	107.85	108.06	108.11	108.13
70	106.2	106.64	107.7	107.75	108.1	107.64
84	104.52	104.73	105.29	105.64	105.85	105.87

Table 2. Sulphate measurement in salt water.

Time (Days)	Sulphate (mg/l)					
	Pt 1	Pt 2	pt 3	Pt 4	Pt 5	Pt 6
1	84.06	83.74	83.65	82.9	82.61	81.12
14	78.1	78.8	79.3	79.52	80	80.05
28	76.12	76.5	77.08	77.25	77.3	77.38
42	74.32	74.67	75.19	75.33	75.6	75.8
56	73.26	73.3	73.6	73.89	73.97	74.09
70	72.88	72.95	72.97	73.08	73.13	73.2
84	72.16	72.37	72.5	72.76	72.8	72.85

Variation in Nitrate Concentration

Pt 1 (0m), pt 2 (0.25m), pt 3 (0.5m), pt 4 (0.75), pt 5 (1m) and pt 6 (1.25).

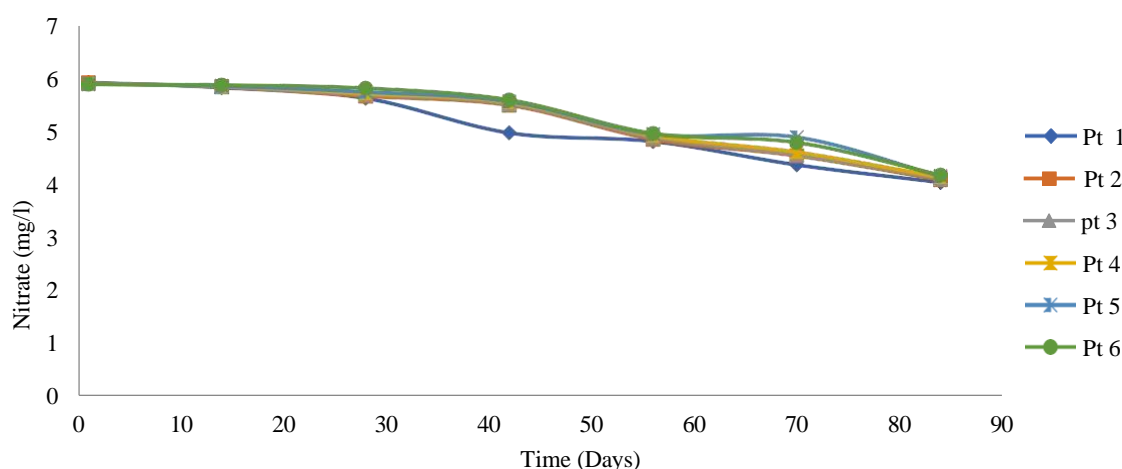


Figure 3. Variation of nitrate in the polluted stagnant fresh water.

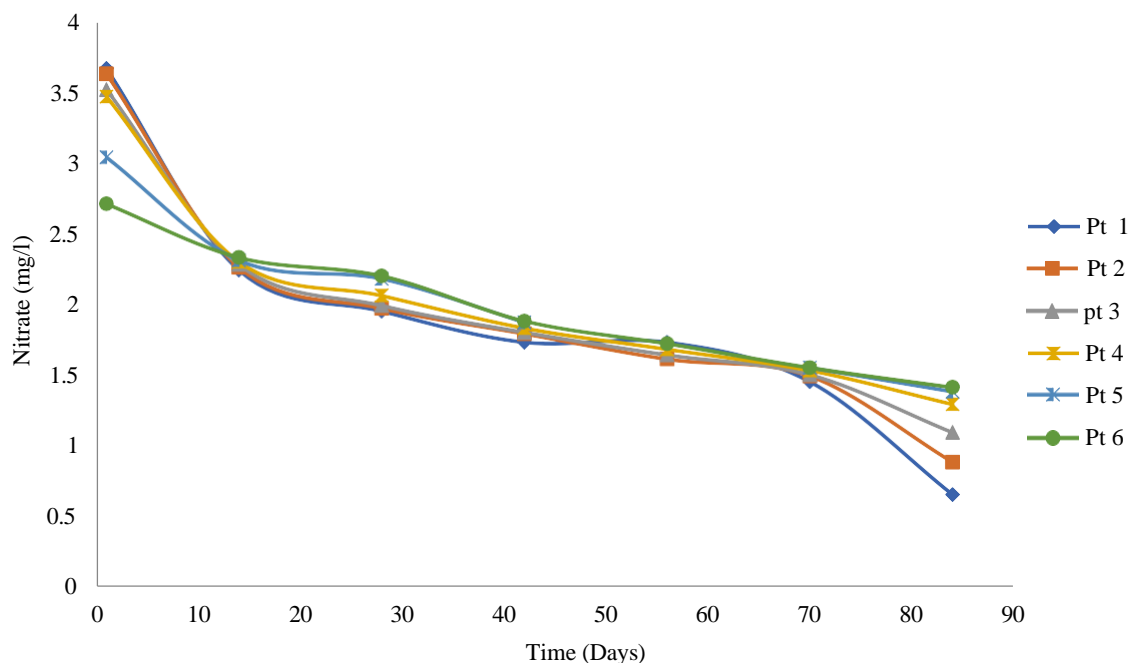


Figure 4. Variation of nitrate in the polluted stagnant salt water.

Pt 1 (0m), pt 2 (0.25m), pt 3 (0.5m), pt 4 (0.75), pt 5 (1m) and pt 6 (1.25).

Figure 3 illustrate the profile of nitrate content with time at different depths for the polluted water media while Figure 4 show the profile of nitrate in relation to time in the polluted salt water.

Table 3. Nitrate measurement in fresh water.

Time (Days)	Nitrate (mg/l)					
	<i>Pt 1</i>	<i>Pt 2</i>	<i>pt 3</i>	<i>Pt 4</i>	<i>Pt 5</i>	<i>Pt 6</i>
1	5.93	5.92	5.91	5.9	5.9	5.89
14	5.83	5.84	5.85	5.86	5.86	5.88
28	5.63	5.67	5.7	5.72	5.75	5.82
42	4.98	5.5	5.53	5.55	5.57	5.6
56	4.82	4.86	4.9	4.93	4.96	4.97
70	4.38	4.55	4.57	4.62	4.9	4.8
84	4.05	4.1	4.13	4.15	4.17	4.19

Table 4. Nitrate measurement in salt water.

Time (Days)	Nitrate (mg/l)					
	<i>Pt 1</i>	<i>Pt 2</i>	<i>pt 3</i>	<i>Pt 4</i>	<i>Pt 5</i>	<i>Pt 6</i>
1	3.67	3.63	3.52	3.47	3.04	2.71
14	2.24	2.26	2.28	2.3	2.31	2.33
28	1.95	1.97	1.99	2.06	2.18	2.2
42	1.73	1.79	1.8	1.83	1.87	1.88
56	1.73	1.61	1.64	1.68	1.7	1.72
70	1.45	1.49	1.5	1.53	1.55	1.55
84	0.65	0.88	1.09	1.29	1.38	1.41

Variation in Turbidity

Pt 1 (0m), pt 2 (0.25m), pt 3 (0.5m), pt 4 (0.75), pt 5 (1m) and pt 6 (1.25).

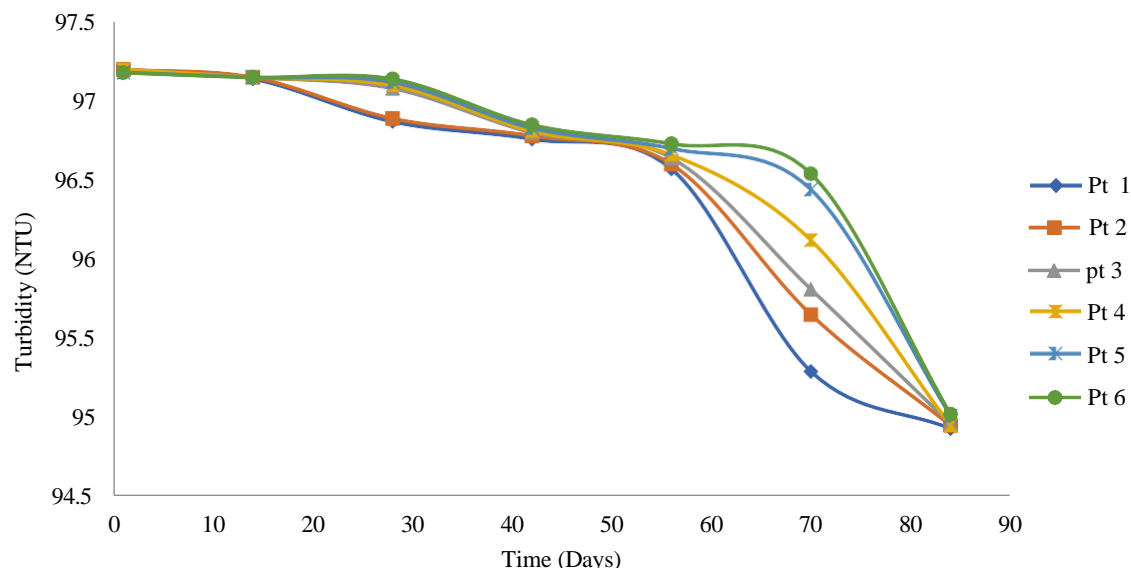


Figure 5. Variation of turbidity in the polluted stagnant fresh water.

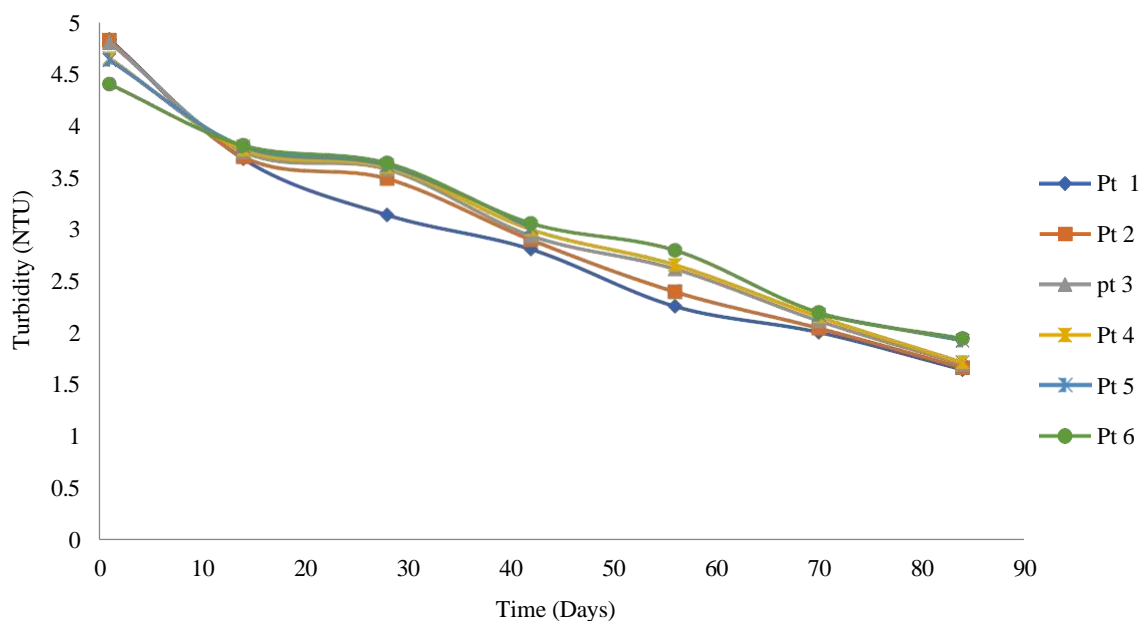


Figure 6. Variation of turbidity in the polluted stagnant salt water.

Pt 1 (0m), pt 2 (0.25m), pt 3 (0.5m), pt 4 (0.75), pt 5 (1m) and pt 6 (1.25).

Figure 5 shows the profiles of turbidity with time at various depths for polluted fresh water. Also, Figure 6 shows the profiles of turbidity with time in polluted salt water. Before crude oil pollution, turbidity in fresh water was recorded as 58.74 NTU and 3.55 NTU in salt water, but after pollution, it increased to 97.2 NTU in the fresh water and 4.83 NTU in the salt water. Turbidity in fresh and salt water decreased with increase in time and marginally increased with increased in depth. Turbidity across the sampling points over the period of the analysis ranged between 94.93 NTU and 97.2 NTU

in fresh water and 1.65 NTU and 4.83 NTU in salt water. The results for turbidity are shown in Tables 5 and 6.

Table 5. Turbidity measurement in fresh water.

Time (Days)	Turbidity (NTU)					
	Pt 1	Pt 2	pt 3	Pt 4	Pt 5	Pt 6
1	97.2	97.2	97.2	97.2	97.18	97.18
14	97.14	97.15	97.15	97.15	97.15	97.15
28	96.87	96.89	97.08	97.1	97.12	97.14
42	96.76	96.78	96.8	96.81	96.83	96.85
56	96.57	96.6	96.64	96.66	96.7	96.73
70	95.29	95.65	95.81	96.12	96.44	96.54
84	94.93	94.95	94.96	94.95	95.01	95.02

Table 6. Turbidity measurement in salt water.

Time (Days)	Turbidity (NTU)					
	Pt 1	Pt 2	pt 3	Pt 4	Pt 5	Pt 6
1	4.83	4.82	4.8	4.65	4.63	4.4
14	3.68	3.7	3.75	3.77	3.8	3.81
28	3.14	3.49	3.58	3.6	3.62	3.64
42	2.81	2.9	2.94	3	3.02	3.06
56	2.26	2.4	2.62	2.66	2.67	2.8
70	2.01	2.05	2.12	2.16	2.18	2.2
84	1.65	1.67	1.7	1.72	1.93	1.95

The marginal variation recorded for turbidity across the sampling periods agreed with some studies on impact of turbidity in surface water (Ryan *et al.*, 2012; Adeniji *et al.*, 2017a). However, the level of turbidity obtained especially for fresh water, was higher than the recommended 5.0 NTU by the World Health Organisation (WHO). This implied that the fresh water system is highly polluted. Also, the increase in turbidity after oil pollution can be attributed to soluble and dissolved solids, dust and soil particles that may be attached with the crude oil samples (Greene, 2002; Ryan *et al.* 2012).

Variation in Alkalinity

The alkalinity in the stagnant fresh and salt water samples determined over the period of the experimental investigation is shown in Figures 7 and 8.

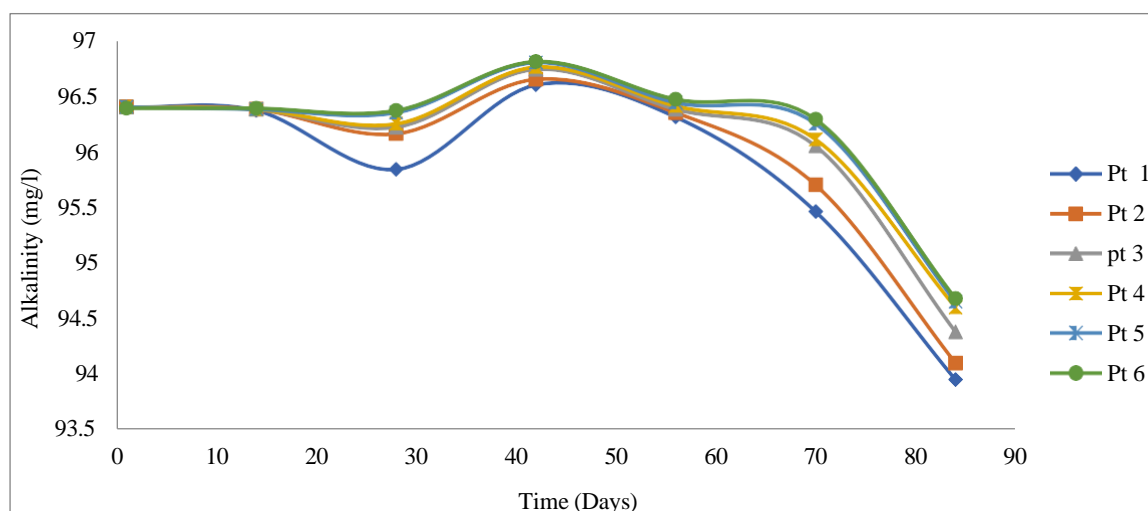


Figure 7. Variation of alkalinity in the polluted stagnant fresh water. Pt 1 (0m), pt 2 (0.25m), pt 3 (0.5m), pt 4 (0.75), pt 5 (1m) and pt 6 (1.25).

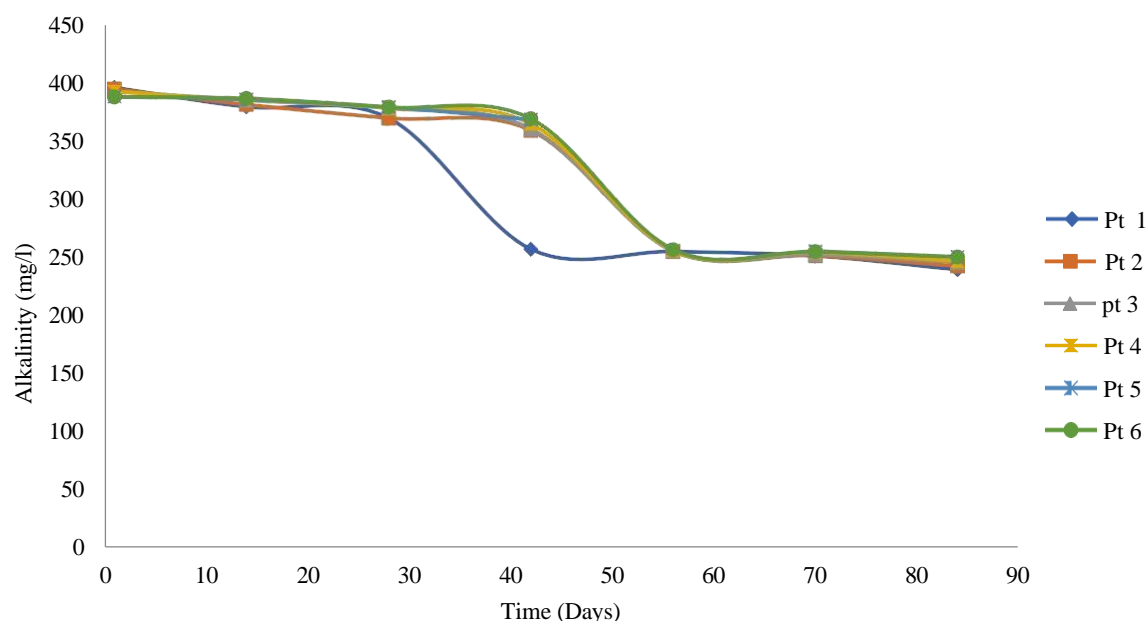


Figure 8. Variation of alkalinity in the polluted stagnant salt water.

Pt 1 (0m), pt 2 (0.25m), pt 3 (0.5m), pt 4 (0.75), pt 5 (1m) and pt 6 (1.25).

Figure 7 demonstrate the profiles of alkalinity in relation to time at various depths for polluted fresh water. While Figure 8 shows the profile alkalinity in relation to time for the contaminated salt water.

Table 7. Alkalinity measurement in fresh water.

Time (Days)	Alkalinity (mg/l)					
	Pt 1	Pt 2	pt 3	Pt 4	Pt 5	Pt 6
1	96.4	96.4	96.4	96.4	96.4	96.39
14	96.37	96.38	96.38	96.38	96.38	96.39
28	95.84	96.16	96.22	96.25	96.35	96.37
42	96.6	96.65	96.74	96.76	96.8	96.81

56	96.31	96.35	96.38	96.41	96.44	96.47
70	95.46	95.7	96.05	96.11	96.25	96.29
84	93.95	94.1	94.38	94.6	94.65	94.68

Table 8. Alkalinity measurement in salt water.

Time (Days)	Alkalinity (mg/l)					
	Pt 1	Pt 2	pt 3	Pt 4	Pt 5	Pt 6
1	396	394.6	392.81	392.52	388.24	387.84
14	379.4	381.4	385.1	385.5	385.7	386.68
28	369.68	369.71	378.2	378.5	379.13	379.2
42	257.2	359.17	360.55	364.79	368.5	369.2
56	255.31	255.4	255.7	256.1	256.8	257
70	251.52	251.74	252.9	254.8	255.62	255.23
84	239.7	242.8	245.92	247.1	250.6	250.66

The increased rate of alkaline reduction in salt water may be as a result of dissolved and soluble ionic compounds present in the salt water (Table 7-8). Since pH is related to alkalinity, it is possible that the hydrogen ions in salt water, alongside volatilization and evaporation of substances, may have initiated biological and chemical reaction thereby resulting to the decreased rate (UNEPGEMS, 2008; Sorlini *et al.*, 2013).

CONCLUSION

The physicochemical parameters of the contaminated water environment revealed difference in increase rate in depth and time. The research also shows that the experimented crude oil has important effect on the properties of the contaminated salt and fresh water environment. All the parameters also decreased with increase in depth except alkalinity, oil & grease, iron and total hardness.

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