Chemical Engineering Journal Storage 4:6 (Desember 2024) 880-902

cejs

Chemical Engineering Journal Storage (CEJS)
home page journal:
https://ojs.unimal.ac.id/cejs/index

Chemical Engineering Journal Storage

PEMERIKSAAN DEGRADASI HIDROKARBON MINYAK BUMI TOTAL PADA MEDIA GARAM DAN AIR TAWAR YANG TERCEMAR

EXAMINATION OF TOTAL PETROLEUM HYDROCARBON DEGRADATION IN A POLLUTED STAGNANT SALT AND FRESH WATER MEDIA

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Abstrak

Tingkat hidrokarbon minyak bumi (TPH) total diperkirakan dalam lingkungan perairan stasioner yang terdiri dari campuran air asin dan air tawar, menggunakan prinsip kinetika orde pertama. Dispersi total petroleum hydrocarbon (TPH) dipelajari dengan adanya air menggunakan model transportasi yang mempertimbangkan variabel konvektif dan difusi. Model ini digunakan untuk memantau konsentrasi TPH baik dalam dimensi vertikal maupun horizontal. Dengan demikian, diantisipasi bahwa difusi secara eksklusif akan mengatur transportasi atau dispersi TPH dalam arah horizontal, sedangkan difusi dan konveksi yang disebabkan oleh gravitasi akan mengatur transportasi TPH dalam arah vertikal. Laju degradasi TPH dianalisis menggunakan kinetika laju degradasi orde pertama dan model Monod. Dalam penelitian ini, kami mensimulasikan dan membandingkan proyeksi degradasi TPH di sepanjang orientasi vertikal dan horizontal. Nilai TPH dalam arah vertikal diperoleh.

Kata Kunci: Total hidrokarbon minyak bumi (TPH), Kinetika orde pertama, Degradasi, Pembersihan, pemeriksaan, Media air

Abstracts

The total petroleum hydrocarbon (TPH) levels were estimated in a stationary aquatic environment that consisted of a mixture of saltwater and freshwater, using the principles of first-order kinetics. The dispersion of total petroleum hydrocarbon (TPH) was studied in the presence of water using a transportation model that considered both convective and diffusion variables. This model was utilised to monitor the concentration of TPH in both the vertical and horizontal dimensions. Thus, it was anticipated that diffusion would exclusively govern the transport or dispersion of TPH in the horizontal direction, while both diffusion and convection induced by gravity would govern TPH transport in the vertical direction. The rate of TPH degradation was analysed using first-order degradation rate kinetics and the Monod model. In this study, we simulated and compared the projected TPH degradation along both vertical and horizontal orientations. The TPH values in the vertical direction were obtained at a specified time and then compared to the experimental data. The purpose of this was to determine the system that best corresponded to the TPH levels measured in the experiment. This study has demonstrated that employing first-order kinetics is a successful approach for monitoring, predicting, and modelling the breakdown of total petroleum hydrocarbons in a stagnant water environment affected by sedimentation.

Keywords: Total petroleum hydrocarbon (TPH), First order kinetics, Degradation, Clean-up, examination, Water media

DOI : https://doi.org/10.29103/cejs.v4i6.19624

1. INTRODUCTION

Water plays a crucial role in both domestic and industrial settings, and changes in its composition are of great interest. Numerous studies have highlighted the impact of petroleum hydrocarbons on the water environment (Amadi et al., 2007;Ukpaka 2006). Research on pollution of subterranean water sources has shown that the dispersion and spread of crude oil significantly affect water quality, often falling below standards for safe use without proper treatment (Yan et al., 2019; Zhi-wei et al., 2000). Therefore, it is essential to monitor the degradation of total petroleum hydrocarbons in polluted stagnant saltwater over time.

Most of the hydrocarbons included in crude oil, such as cycloalkanes, asphaltenes, mono- and polyaromatics, aliphatic (linear or branched) hydrocarbons, and resins, are carcinogenic, poisonous, and stable (Cunningham et al., 2004; Ryan et al.,2001). Petroleum constituents including Alkanes, benzene, toluene, ethyl benzene, and xylenes (BTEX) along with certain polycyclic aromatic hydrocarbons (PAHs) can be broken down through biodegradation in correct weather patterns and marine environments with reduced salt levels (Ryan et al., 2001). Nonetheless, some constituents of petroleum products, such as polycyclic aromatic sulfur heterocyclic (PASH) compounds and bigger molecular PAHs, might not degrade through biodegradation. Non-biodegradable materials continue to pose a serious concern as long as they are in the immediate area.

Thus, petroleum hydrocarbons are significant pollutants in the environment that damage ecosystems. Various substances such as salts, organic compounds, alcohols, phenols, acids, radionuclides, PAHs, and trace metals like zinc, cadmium, and mercury, among others, could potentially be found in soil, groundwater, and wastewater contaminated with oil are significantly differing quantities (Pathak et al., 2010). Dispersants for oil plumes and bioremediation are two methods for reducing the effects of crude oil spills (Al-Rabeh et al., 1989).

(Angle et al., 2001) Conducted extensive research on the fate of petroleum in maritime environments. Releasing crude oil and products derived from petroleum distillation into the water leads to a range of physical, chemical, and biological alterations (APHA 1995). Biological weathering procedures involve vaporization, dissolution, dispersion, photochemical oxidation, emulsification of water in oil, adsorption onto suspended particle substance, descending, and deposition (Atlas 1992). The initial pollutant's physical and chemical makeup may undergo substantial changes due to simultaneous activities, potentially impacting the speed and effectiveness of biodegradation. Several mechanisms impact the way in which petroleum is distributed and its composition when released into the maritime environment. The initial and most crucial stage, spreading, is governed based on the characteristics and composition of the oil, as well as the ambient conditions into which it is released. Spreading is the most important phase for the first 10 hours after a spill.

Spreading is a physical phenomenon that is connected to chemical composition and processes. In an oil spread in a calm maritime environment, Fay identified four main forces or processes: gravitational, surface tension, inertial, and frictional forces. The lateral spreading in the direction of decreasing film thickness is primarily driven by gravitational force. This force is impacted by factors such as the layer's thickness, thickness gradient, and the density variance between water and oil. Another significant force contributing to spreading is the spreading coefficient σ, calculated as the disparity between air-water surface tension and the combined air-oil and oil-water surface tensions. During the final spreading phase, this force, which remains unaffected by film thickness, emerges as the predominant mechanism.

The study focuses on how different components of crude oil are broken down by crude oil degraders in a stationary maritime environment. The goals of this research are to establish the physiochemical parameters of crude oil, fresh water, salt water as well as the polluted fresh and salt water with respect to time, analyse the dispersion of the concentration of total petroleum hydrocarbons changes over time through different depths of water and to develop an efficient and workable predictive model for crude oil, investigate the breakdown process in still water environments and analyse the speed at which sediment settles in stagnant water media using efficient and workable predictive models.

The examination the process of breaking down Total Petroleum Hydrocarbons (TPH) in both polluted still saltwater and freshwater media presents a novel and unique research opportunity. While TPH degradation studies are not uncommon, focusing on both saltwater and freshwater environments adds a new dimension to the research.The degradation of TPH in polluted stagnant saltwater and freshwater media can be influenced by various factors such as microbial activity, temperature, oxygen levels, and the presence of other contaminants. Understanding how TPH degrades in these different environments can provide valuable insights into the effectiveness of bioremediation strategies and the overall impact of petroleum pollution on aquatic ecosystems.

By examining TPH degradation in both saltwater and freshwater media, researchers can gain a more comprehensive understanding of the processes involved and potentially uncover new insights into the biodegradation mechanisms of petroleum hydrocarbons in different aquatic environments. This research could have implications for environmental remediation efforts and help inform strategies for mitigating the impact of petroleum pollution on water bodies.

2. METHODS

The materials required to examine the degradation of crude oil in polluted stagnant salt and fresh water media include :water samples from the polluted sites, TPH standards for calibration, extraction solvents like hexane or dichloromethane, analytical instruments like Gas Chromatography-Mass Spectrometry (GC-MS) for TPH analysis, and microbial cultures for biodegradation studies.

The methods involved would include sample collection and preparation, extraction of TPH from water samples, analysis using GC-MS to quantify TPH levels, and monitoring TPH degradation over time in both salt and fresh water media. Additionally, conduct of biodegradation studies by inoculating the water samples with microbial cultures and monitoring TPH degradation rates.

Crude oil samples were acquired from the Port Harcourt Refinery Company and then transferred to River State University for analysis. Gas chromatography was utilized to examine the samples for bacterium species presence and to detect any changes in the oil's composition and physiochemical properties. Saltwater samples were gathered from Ntawaba Creek on Eagle Island in the Port-Harcourt Local Government Area of Rivers State, while freshwater samples were sourced from Orashi Rivers in Omoku Town, Ogba/Egbema/Ndoni Local Government Area of Rivers State. The bulk water was divided into various points or segments, and samples were randomly taken using a sampler. These samples were then transported to the Rivers State University Chemical/Petro-Chemical Laboratory through manual and composite sampling methods.

The supplied samples were poured into two 1,500-liter batch reactors that were made or manufactured in a cylindrical shape and had six plastic taps spaced 25 centimeters apart. There were two batch reactors as shown in Figure 1 and Figure 2, one for fresh water and one for salt water. In order to maintain sample integrity, the sampling procedures were repeated multiple times in compliance with the custody protocol until the two batch reactors were completely filled with fresh and salt water, respectively.

To create a homogeneous mixture, the two batch reactors holding fresh water and salt, respectively, were shaken violently. Samples were then taken from each reactor for studies of their total petroleum hydrocarbon content, total bacteria count, and physicochemical properties (Table 1).

Figure 1. Experimental set-up of cylindrical batch reactor: GP tank with uniformly spaced control valves for collection of samples

Figure 2. Pollution of fresh and salt water by crude oil

Table 1. Physicochemical parameters and method of analysis

S/N	Variables	Test Method
1.	Complete Dissolved Solid (mg/L)	APHA 2510B
2.	Conductivity (μS/cm)	APHA 2510B
3.	Temperature (ºC)	APHA 4500T
4.	P^H	APHA 4500T
5.	Chloride (mg/l)	APHA 4500HB
6.	Sulphate (mg/l)	APHA 4500
7.	Nitrate (mg/l)	EPA 3521
8.	Turbidity (NTU)	APHA 2130B
9.	Alkalinity (mg/l)	ASTM D 1067
10.	Oil and grease (mg/l)	APHA 3111B
11.	Dissolved oxygen (mg/l)	ASTM D 3921
12.	Iron (mg/l)	APHA 3111B
13.	Overall Hardness (mg/l)	APHA 2340C
14.	Overall suspended Solif (mg/L)	APHA 2340C

Solution to the Model

Model solution can be evaluated through quantitative or analytical method. In this research, the analytical approach was utilized, employing the method of transformation. Initially, the equation is simplified through the utilization of the substitution technique as described by (Yadav et al., 2011). This procedure is explained as:

$$X = z + r\sqrt{\left(\frac{D_r}{D_z}\right)} \tag{1}$$

Through this replacement, the concentration, denoted as C, is now dependent on X. Therefore, the relationship can be expressed as follows:

$$\frac{\partial C}{\partial r} = \frac{\partial C}{\partial X}.\frac{\partial X}{\partial r} \tag{2}$$

When equation (2) is differentiated directly with respect to r, the result becomes:

$$\frac{\partial X}{\partial r} = \sqrt{\frac{D_r}{D_z}} \tag{3}$$

Now, combining equations (1) and (3) gives:

$$\frac{\partial C}{\partial r} = \sqrt{\frac{D_r}{D_z}}\frac{\partial C}{\partial X}$$

In the same manner, if C is dependent on z as well, the following relationship can be observed:

$$\frac{\partial C}{\partial z} = \frac{\partial C}{\partial X}.\frac{\partial X}{\partial z} \tag{4}$$

Once more, when equation (1) is differentiated directly with respect to z, the result is obtained.

$$\frac{\partial x}{\partial z} = 1 \tag{5}$$

Therefore, equation (5) transforms into:

$$\frac{\partial C}{\partial z} = \frac{\partial C}{\partial X} \tag{6}$$

Expanding on equation (6) by taking the derivative with respect to r yields the following result.

$$\frac{\partial^2 C}{\partial r^2} = \sqrt{\frac{D_z}{D_r}}\frac{\partial^2 C}{\partial X^2} \tag{7}$$

Additionally, when equation (7) is further differentiated with respect to r, the result is.-

$$\frac{\partial^2 C}{\partial z^2} = \frac{\partial^2 C}{\partial X^2} \tag{8}$$

$$\frac{\partial C}{\partial t} = -v_r\sqrt{\frac{D_r}{D_z}}\frac{\partial C}{\partial X} - v_z\frac{\partial C}{\partial X} + D_r\sqrt{\frac{D_r}{D_z}}\frac{\partial^2 C}{\partial X^2} + D_z\frac{\partial^2 C}{\partial X^2} - R_i \tag{9}$$

Simplification of equation (9) gives:

$$\frac{\partial C}{\partial t} = \left(D_r\sqrt{\frac{D_r}{D_z}} + D_z\right)\frac{\partial^2 C}{\partial X^2} - \left(v_r\sqrt{\frac{D_r}{D_z}} + v_z\right)\frac{\partial C}{\partial X} + -R_i \tag{10}$$

Equation (11) is further simplified as:

$$\frac{\partial C}{\partial t}=D\frac{\partial^2 C}{\partial X^2}-v\frac{\partial C}{\partial X}+-R_i(C) \qquad (11)$$

where:

$$D=\left(D_r\sqrt{\frac{D_r}{D_z}}+D_z\right)$$

$$v=v_r\sqrt{\frac{D_r}{D_z}}+v_z$$

Using the boundary conditions

$$t\ =\ 0 \qquad 0<X<\infty\ ; \quad C\ =\ 0 \qquad (12)$$

$$t\ >\ 0 \qquad X=\infty; \quad C\ =\ 0 \qquad (13)$$

$$t\ >\ 0 \qquad X\ =\ 0\ ; \quad C\ =\ C_o \qquad (14)$$

$\lambda\left(X,t\right)$, as per the research conducted by [12], $\lambda\ and\ C$ and are connected through a transformation that can be represented as :

$$C(X,t)\ =\lambda(X,t)\exp\left\{\frac{v}{2D}X-\left(\frac{v^2}{4D}+R_i(C)\right)t\right\} \qquad (15)$$

When equation (15) undergoes the Laplace transform, the resulting expression is:

$$s\overline{C}-C_{(o)}=D\frac{\partial^2\overline{C}}{\partial X^2}-V\frac{\partial\overline{C}}{\partial X}-\overline{R_i}(C)$$

$$\therefore\ \ s\overline{C}\ =\ D\frac{\partial^2\overline{C}}{\partial X^2}-V\frac{\partial\overline{C}}{\partial X}-\overline{R_i}(C) \qquad (16)$$

When the BC is applied, X =0 and t = 0, equation (16) is transformed .

$$C(0,0)=\lambda(0,0) \qquad (17)$$

Thus, the LT of equation (17) gives

$$\overline{C}\ \ =\ \overline{\lambda} \qquad (18)$$

Therefore, equation (18) can be written as

$$S\overline{\lambda}-D\frac{\partial^2\overline{\lambda}}{\partial X^2}-V\frac{\partial\overline{\lambda}}{\partial X}-\overline{R_i}(C) \qquad (19)$$

Again, when $t=0\ and\ \frac{\partial\lambda}{\partial X}=0$, equation (19) becomes

$$S\bar{\lambda} = D\frac{d^2\bar{\lambda}}{\partial X^2} \tag{20}$$

It was observed that equation (20) follows a general form:

$$\frac{d^2 y}{dx^2} - n^2 y = 0 \tag{21a}$$

And solution is

$$A\,e^{nx} + Be^{-nx} \tag{21b}$$

Therefore, equation (21) becomes:

$$\bar{\lambda} = Ae^{\sqrt{s/D}X} + Be^{-\sqrt{s/D}X} \tag{22}$$

Applying the BC:

When $X = \infty,\ \lambda = 0\ \therefore\ \bar{\lambda} = 0\ and\ A = 0$

When $X = 0\ and\ t > 0,$ we have from equation (22)

$$C_o = \lambda e^{-\left(\frac{v^2}{4D} + R_i(C)\right)t}$$

$$\therefore \qquad \lambda = C_o e^{\left(\frac{v^2}{4D} + R_i(C)\right)t} \tag{23}$$

The LT of equation (23) is

$$\bar{\lambda} = \frac{C_o}{s - \left(\frac{v^2}{4D} + R_i(C)\right)} \tag{24}$$

From equation (24), in the case where A = 0

$$\bar{\lambda} = Be^{-\sqrt{s/D}\,X}$$

and at $X = 0$

$$B = \frac{C_o}{s - \left(\frac{v^2}{4D} + R_i(C)\right)} \tag{25}$$

Substituting $B\ and\ A$ into equation (25) gives

$$\bar{\lambda}(X,s) = \frac{C_o}{s - \left(\frac{v^2}{4D} + R_i(C)\right)} e^{-\sqrt{s/D}\,X} \tag{26}$$

To convert a function from the Laplace domain to the time domain, the inverse Laplace transform of equation (26) was applied to obtain the below equation.

$$L^{-1}\left[\lambda(X,s)\right] = L^{-1}\left[\frac{C_o}{s - \left(\frac{v^2}{4D} + R_i(C)\right)} e^{-\sqrt{s/D}\,X}\right]$$

From Laplace table and conducting additional simplifications, we obtain:

$$\lambda(X,t) = \frac{C_o}{2}\left\{erfc\left[\frac{X - (v + R_i(C))t}{2\sqrt{Dt}}\right] + erfc\left[\frac{X + (v + R_i(C))t}{2\sqrt{Dt}}\right]\right\} \tag{27}$$

$$C(X,t) = \frac{1}{2}C_o\left\{erfc\left[\frac{X - (v + R_i(C))t}{2\sqrt{Dt}}\right] + erfc\left[\frac{X - (v + R_i(C))t}{2\sqrt{Dt}}\right]\right\}\exp\left[\frac{v}{2D}X - \left(\frac{v^2}{4D} + R_i(C)\right)t\right]$$

The equation (27) was modified by incorp incorporating the rate term, where the assessment of TPH concentration in the stagnant water system was conducted using tests on the first order degradation rate and Monod equations.

The speed at which oil particles settle down the column.

The research focused on examining the speed at which oil particles descended through a column of still water using a specific model. Initially, a broad concept introduced by (Ukpaka et al., 2011) regarding the sedimentation of suspended solid particles, affected by the on-going release of waste in a pond system, was adjusted by incorporating the principles of Stokes and Newton concerning particles descending into a fluid system(Ukpaka et al., 2011).

$$R_s = \frac{v_s}{z} C_{ss} \tag{28}$$

After exploring various mathematical relationships concerning key parameters, [13] ultimately formulated the sedimentation rate as:

$$R_s = \left[U - \exp\left(\frac{1}{gS_o z} \cdot \frac{v_s^2}{1 - v_s} \right) \right] \frac{v_s}{z} \tag{29}$$

where:

$R_s =$ The speed at which a particle settles (mg/l.day)

$U =$ The speed at which momentum is transferred (kg.m/day)

$C_{ss} =$ Amount of suspended particles in a given volume of liquid (mg/l)

$g =$ The acceleration experienced by an object due to the force of gravity (m/s^2)

$S_o =$ Underneath the water's surface incline (-)

$z =$ The distance of the sample point from the surface of the water (m)

$v_z =$ Settling velocity (m/s)

The speed of sedimentation determined by Stokes' law

The settling velocity in this scenario was determined using the principles of Stokes' law, which can be defined as:

$$v_s \propto gD_p^2 \left(\frac{\rho_p - \rho_f}{18\mu} \right) \tag{30}$$

When the proportionality is eliminated, the result is as follows:

$$v_s = k_F g D_p^2 \left(\frac{\rho_p - \rho_f}{18\mu} \right) \tag{31}$$

As the oil volume can be measured, the particle diameter D_p was described in relation to the volume of the oil particle. Therefore, it is assumed that the oil particle has a spherical shape. The formula to calculate the volume of a sphere is :

$$V = \frac{\pi D_p^3}{6} \tag{32}$$

Therefore, when considering particle size, equation (32) could be expressed as:

$$D_p = \left(\frac{6V}{\pi} \right)^{1/3} \tag{33}$$

$$v_s = k_F g \left(\frac{6V}{\pi} \right)^{2/3} \left(\frac{\rho_p - \rho_f}{18\mu} \right) \tag{34}$$

$$R_s = K_F g V^{2/3}\left(\frac{\rho_p - \rho_f}{18\mu}\right)\frac{C_{TSS}}{z} \tag{35}$$

3. Results and Discussion (12 pt, bold, capital letters)

Table 2. Test results

S/no	Parameters	Test method	Result	Standard
1	Total Dissolved Solids (mg/l)	APHA 2510 B	31	500
2	Conductivity (µS/cm)	APHA 2510 B	36.90	-
3	Temperature (ºC)	APHA 4500 B	26.18	-
4	P^H	APHA 4500 HB	6.83	6.5-8.5
5	Chloride (mg/l)	APHA 4500 C	59.50	250
6	Sulphate (mg/l)	APHA 4500 SO_4^{2-}	38.45	400
7	Nitrate (mg/l)	EPA 3521	1.36	40
8	Turbidity (NTU)	APHA 2130 B	58.74	5
9	Alkalinity (mg/l)	ASTM D1067	30.10	400
10	Oil & Grease (mg/l)	APHA 3111 B	7.86	10
11	Dissolved Oxygen (mg/l)	ASTM D3921	8.60	7
12	Iron (mg/l)	APHA 3111 B	0.28	0.3
13	Complete firmness (mg/l)	APHA 2340 C	53.90	500
14	Overall suspended Solid (mg/l)	APHA 2340 C	26.72	-

Table 3. Evaluated Monod Constants in Fresh and Salt Water

	Fresh Water		Salt Water	
	Um	Ks	Um	Ks
PT1	38.1679	23928.2	11.0988	15498.3
PT2	4.64253	7625.81	8.88099	5354.44
PT3	29.7619	6595.24	11.3895	3865.03
Average	24.1908	12716.4	10.4564	8239.27

Table 4 Diffusion Coefficient in Fresh and Salt Water

Depth (m)	*D* (m^2/day)
0.25	1.7464×10^{-4}
0.5	1.3971×10^{-4}
0.75	1.0479×10^{-4}
1.0	6.9857×10^{-5}
1.25	3.4928×10^{-5}

The graphs in Figures 3 and 4 show the calculations of the initial rate constant for freshwater and saltwater settings. The rate constants for PT1, PT2, and PT3 were determined as 0.0029, 0.0030, and 0.0043day-1, respectively, using the linear equations in Figure 5, with an average of 0.0034day-1 for freshwater. Furthermore, based on the linear equations in Figure 6, the rate constants for PT1, PT2, and PT3 were found to be 0.0011, 0.0025, and 0.0028 days-1, respectively, averaging at 0.00213 days-1.

Similarly, the plots used to calculate the Monod constants for freshwater and saltwater media, respectively, are displayed in Figures 3 and 4. The highest specific rate constant, Um, was determined using the linear equations in Figures 5 and 6, and it was found to be 38.1679, 4.6424, and 29.7619 mg/l.day at PT1, PT2, and PT3, respectively. For fresh water, this equaled an average of 24.1908 mg/l. For fresh water, the Monod rate constant was calculated as 23928.2, 7625.81, and 6595.24 mg/l, with an average of 12716.43 mg/l. The Monod constant values were determined to be 15498.3, 5354.44, and 3869.03 mg/l, with an average of 8239.27 mg/l. The maximum precise rate constant, Um, was found to be 11.0988, 8.8810, and 11.3895 mg/l.day at PT-1, PT-2, and P-T3, respectively. In salt water, the average optimal precise rate constant Um was found to be 10.4564mg/l, with values of 11.0988, 8.8810, and 11.3895 mg/l.day at PT-1, PT-2, and PT-3 respectively. The Monod constant Table 3, computed 8239.27mg/l, with individual values of 15498.3, 5354.44, and 3869.03 mg/l. Based on experimental results, the diffusion coefficient, or D, in the vertical direction in the aqueous medium was also calculated. Diffusion coefficient, Table 4, varied with depth, as revealed by the analysis. As a result, at 0.25 meters, the diffusion coefficient dropped from 1.7464×10^{-4} to 3.4928 x 10-5. The estimated constants were used to simulate the diffusion model and forecast the vertical and horizontal TPH concentration in the water medium. This implies that the rate of sedimentation of suspended solids in crude polluted stagnant fresh and salt water decreased with increase in depth and time. Therefore, the rate at which suspended solids entrained in crude oil settle on the base of stagnant water media is highly dependent on the depth and specified time.

The result of the research is of great significance in the environmental sustainability of the crude oil polluted stagnant water media especially clean-up processes. Most of clean up processes are surface oriented , that is targeted towards the concentration of the crude oil at surface with little or no attention to the concentration of the crude along the depth of the water table.

The analysis using GC-MS chromatography enabled us to identify the component profiles of TPH-contaminated water. The chromatographic profiles of the water sample can be seen in (Fig.7). The peaks and their retention times (RT) on the chromatogram represent the various compounds present in the sample, Table 5. These compounds were identified by comparing their retention time and mass spectra with the mass spectrum library. The breakdown of hydrocarbons found in each sample can be found in Table 5. The sample predominantly consists of straight-chain alkanes, which are reflected in the tallest peaks on the chromatograms, as well as branched alkanes with retention times matching the peaks inside the chromatograms. The most common straight-chain alkanes ranged from n-C8 to n-C12, n-C15, n-C20, and n-C27. The most commonly identified compounds were polycyclic aromatic hydrocarbons (PAH) like acenaphthene, along with straight-chain alkanes and isoalkanes including pristane and phytane.

Straight-chain alkanes can be found in natural sources such as crude oil and natural gas deposits, as well as in petroleum products and fossil fuels. Branched alkanes are commonly found in petroleum products and are also produced during the combustion of fossil fuels. Polycyclic aromatic hydrocarbons (PAHs) are formed during incomplete combustion of organic materials such as coal, oil, and gas, as well as from natural sources like forest fires and volcanic eruptions.

These hydrocarbons can have significant environmental impacts, as they are often toxic and can persist in the environment for long periods of time. Straight-chain alkanes and branched alkanes can contaminate water sources through spills or leaks from oil and gas operations, while PAHs can be released into water bodies through runoff from urban areas, industrial activities, and contaminated soil.

In terms of water quality assessment, the presence of these hydrocarbons in water can indicate pollution and potential health risks for aquatic organisms and humans. Monitoring levels of straight-chain alkanes, branched alkanes, and PAHs in water can help assess the impact of human activities on water quality and guide remediation efforts to protect ecosystems and public health.

Freshwater bodies tend to have lower concentrations of dissolved salts compared to saltwater bodies. Freshwater typically has an average salinity of less than 0.5 parts per thousand (ppt), while saltwater bodies such as oceans have an average salinity of around 35 ppt. The differences in salinity between freshwater and saltwater can have significant implications for the types of organisms that can thrive in these environments. Freshwater ecosystems support a wide variety of freshwater species adapted to lower salinity levels, while saltwater ecosystems are home to marine species that have evolved to tolerate higher salinity levels.

From these comparisons, we can draw conclusions about the unique characteristics and biodiversity of freshwater and saltwater ecosystems. Freshwater ecosystems are more vulnerable to changes in salinity levels due to their lower salt content, while saltwater ecosystems are more stable in terms of salinity but face challenges related to ocean acidification and pollution.

The variation of the diffusion coefficient with depth can be influenced by several factors, including temperature, pressure, salinity, and the presence of other dissolved substances in the water. In general, the diffusion coefficient tends to decrease with increasing depth in water bodies due to changes in these environmental factors. The drop in the diffusion coefficient from 1.7464 x 10-4 to 3.4928 x 10-5 at 0.25 meters could be attributed to a change in temperature, salinity, or the presence of dissolved substances at that specific depth. For example, a decrease in temperature with depth can lead to a decrease in the diffusion coefficient, as lower temperatures can slow down the movement of molecules in water. Similarly, changes in salinity or the presence of other dissolved substances can also affect the diffusion coefficient at different depths.

It is important to consider the specific environmental conditions at each depth to understand why the diffusion coefficient dropped at 0.25 meters. Conducting further analysis and measurements of these factors at different depths can help provide a more comprehensive explanation for the observed variation in the diffusion coefficient. Understanding the differences in average values for freshwater and saltwater can help inform conservation efforts and management strategies to protect and preserve these valuable ecosystems for future generations.

To evaluate the accuracy of simulated results in predicting TPH concentrations, it is essential to compare the model predictions with actual field measurements taken at the same locations and under similar conditions. Any significant differences between the predicted and measured values should be carefully analyzed to identify potential sources of error or uncertainty in the simulation process. The examination of Total Petroleum Hydrocarbon (TPH) degradation in polluted stagnant salt and freshwater media presents promising future prospects and novelty in the field of environmental remediation and pollution control. By studying the degradation of TPH in both saltwater and freshwater environments, researchers can gain valuable insights into the effectiveness of bioremediation techniques in different aquatic settings. Understanding how TPH degrades in stagnant salt and freshwater media can help develop targeted strategies for cleaning up contaminated water bodies and restoring ecosystem health.

The novelty of this study lies in its focus on comparing TPH degradation in two distinct environments - saltwater and freshwater. This comparative analysis can provide new knowledge on the factors influencing TPH degradation rates, the role of microbial communities in biodegradation processes, and the potential for using natural processes to remediate petroleum-contaminated water bodies. Overall, the study of TPH degradation in polluted stagnant salt and freshwater media holds great promise for advancing our understanding of bioremediation techniques and their application in diverse aquatic environments. The findings from this research can inform future pollution control strategies and contribute to the development of sustainable solutions for addressing petroleum contamination in water resources.

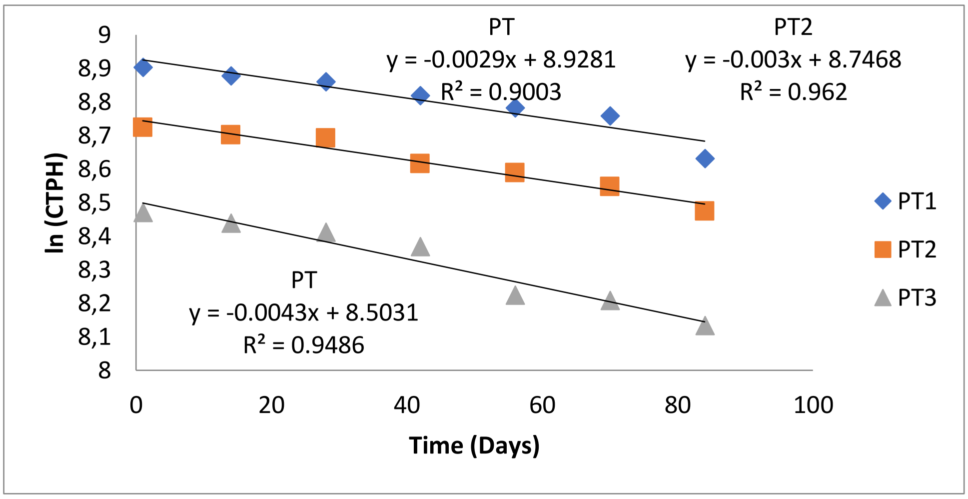


Figure 3. Kinetic plots of first order for the estimation of the rate constant of fresh water use

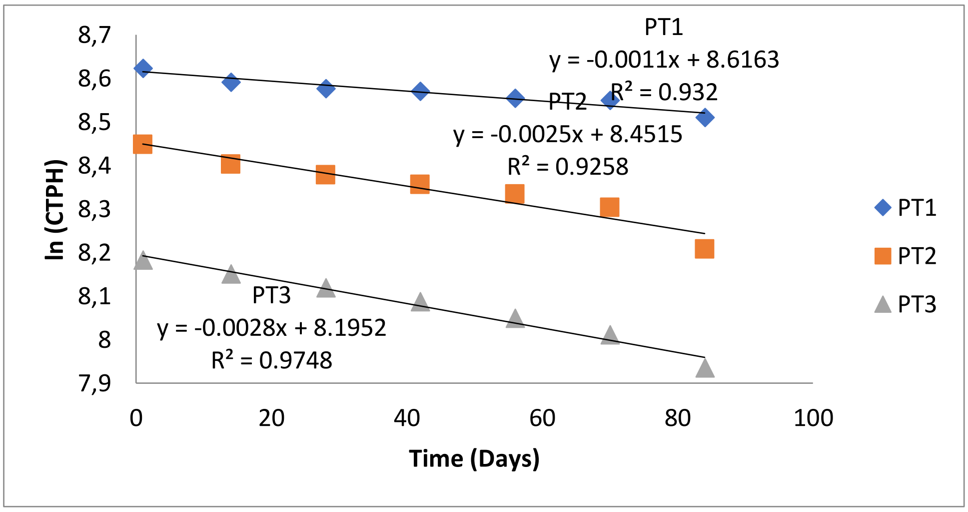


Figure 4. The rate constant for salt water determined using first-order rate kinetic graphs

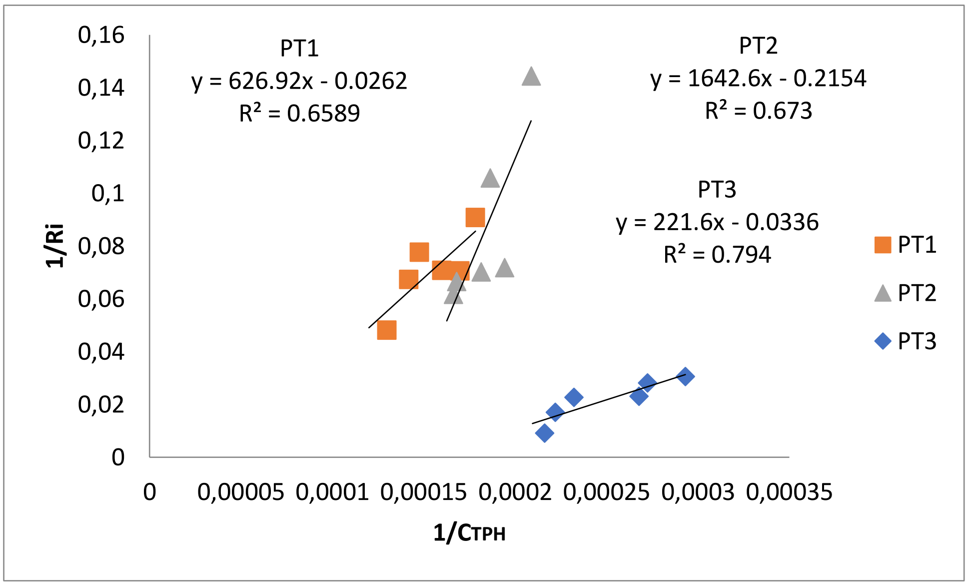


Figure 5. Fresh water rate constants determined using line waver-Burke plots

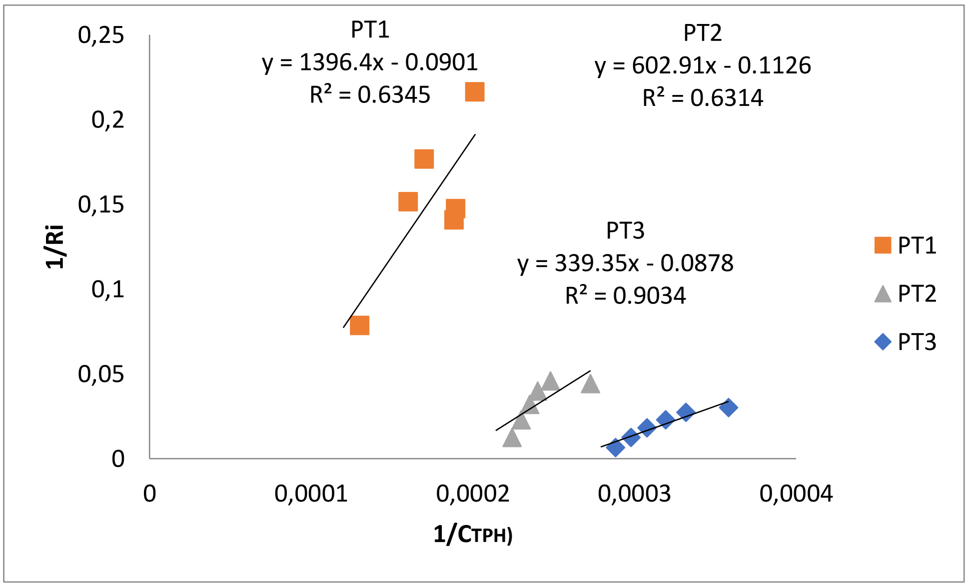
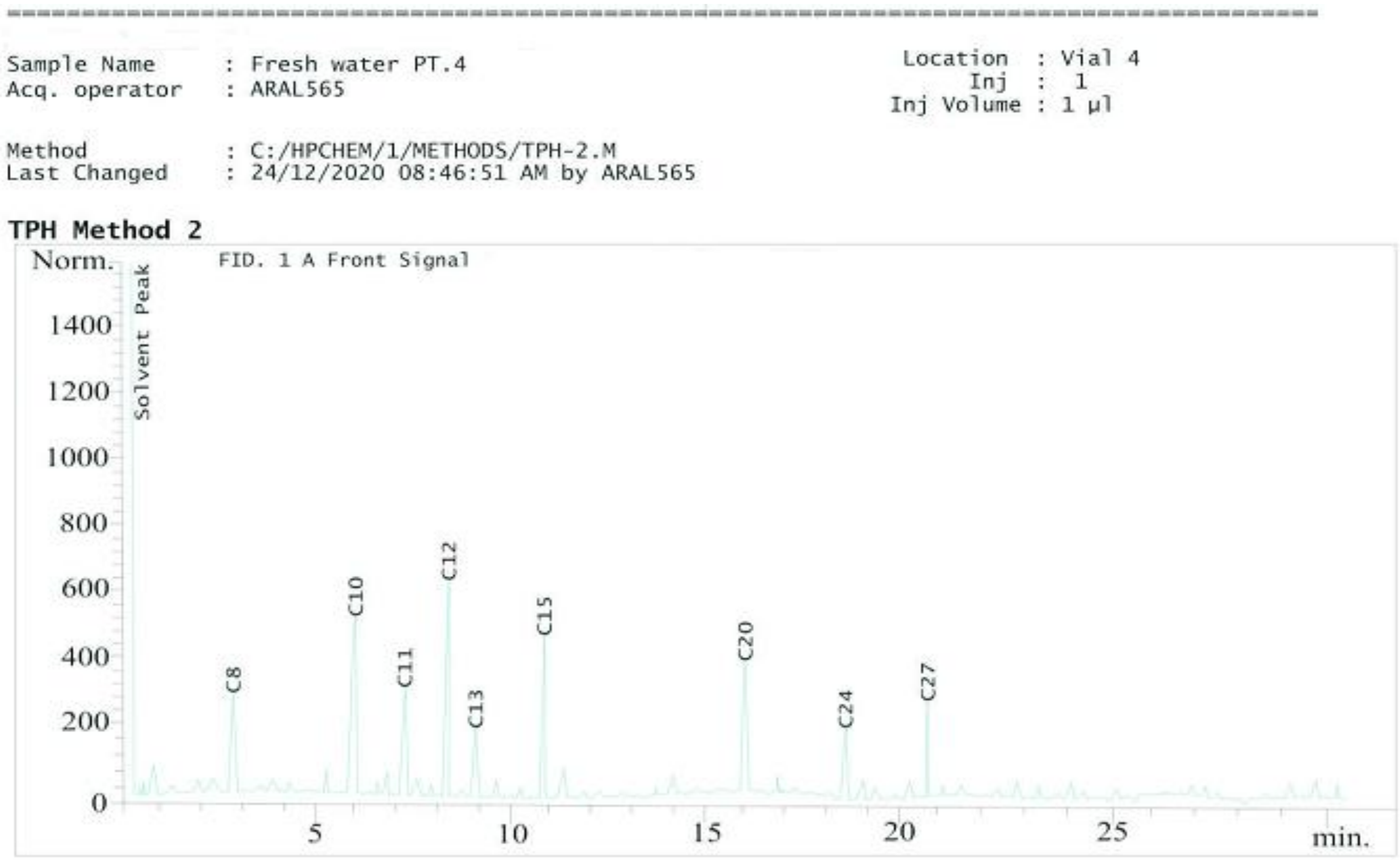


Figure 6. Rate constants for salt water calculated using line waver-Burke plots



```
Sample Name     : Fresh water PT.4                    Location  : Vial 4
Acq. operator   : ARAL565                                  Inj  :  1
                                                      Inj Volume : 1 µl

Method          : C:/HPCHEM/1/METHODS/TPH-2.M
Last Changed    : 24/12/2020 08:46:51 AM by ARAL565
```

TPH Method 2

Fig.7. The chromatographic profiles

Table 5 GC-MS result

Ret. Time(min)	Type	Area	Amt/Area	Amount [ppm]	Grp Name
4.351	W	46.54703	3.24534e-1	216.43498	C8
6.35	-	-	-	-	C9
6.553	W	73.54218	5.01309e-1	473.15841	C10
6.635	W	51.84039	3.47847e-1	286.05039	C11
7.562	W	79.32025	7.04958e-1	591.54318	C12
9.327	W	47.84574	3.06121e-1	126.20116	C13
9.402		-	-	-	C14
11.940	W	53.12745	6.03294e-1	408.64383	C15

12.232	-	-	-	-	C16
15.138	-	-	-	-	pr
15.282	-	-	-	-	C17
17.598	-	-	-	-	C18
18.105	-	-	-	-	ph
20.249	-	-	-	-	C19
20.580	W	52.73469	5.13193e-1	331.50431	C20
20.869	-	-	-	-	C21

4. CONCLUSIONS

The three models showed that as depth increased, the rate of sedimentation reduced. The model that incorporates Newton's law shows the least sedimentation rate, while the modified Stokes' law follows with a moderate rate, and Ukpaka exhibits the highest sedimentation rate. All three of the sedimentation models have the potential to be utilized to investigate the pace at which oil sediment settles in stagnant water media, despite the minor variations in their performances. The study finds that TPH was degraded at all PT1, PT2, and PT3 sampling points, and that it degraded quickly at PT-3 > PT-2 > PT-1, indicating the existence of extremely obligate anaerobes. The breakdown of total petroleum hydrocarbons also shows a trend that suggests that first-order kinetics involves reliable method for forecasting the process, it was regulated by violating the physicochemical parameters of the process. Finally, a comparison shows that TPH degrades more quickly in salt media than in fresh water medium.The number of carbon in this sample ranged from C8 to C21 for linear alkanes and from C15 to C20 for highly branched alkanes. Shorter chain hydrocarbons (< C13) are generally readily degraded because of their lower molecular weight and water solubility, whereas medium-length alkanes (C8–C12), and long-chain alkanes (>C12) are degraded at a relatively slow rate.

5. ACKNOWLEDGMENTS

In this section, the author may acknowledge any support given, such as funding and the name of the expert that the author discussed in the manuscript.

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