ENVIRONMENTAL ENGINEERING

Evaluation of Temperature Effects on Biokinetic Functional Parameters of Petroleum Hydrocarbon Degradation in Freshwater Environment

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Abstract

This study investigated the influence of temperature on the biokinetic functional parameters governing total petroleum hydrocarbon (TPH) degradation in freshwater environments. The research employed the Monod kinetic model to describe the relationship between substrate concentration and degradation rate, while Lineweaver–Burk analysis was used to evaluate the maximum specific degradation rate and substrate affinity-related kinetic constant. Temperature-dependent kinetic behaviour was examined at 15, 30, 45, 60 and 75 °C. The reciprocal relationship between degradation velocity and substrate concentration was evaluated using linear regression equations obtained from the corresponding Lineweaver–Burk plots. The estimated maximum velocity parameters (Vmax) varied considerably with temperature, with reported values of 285.71, 333.33, 1666.67, 500, 500, 50,000 and 166.67 $(ppm/hr)^{-1}$ at 15, 30, 45, 60 and 75 °C, respectively. The corresponding reported kinetic constants also exhibited substantial variations, indicating a temperature-dependent response of the degradation system. In addition, modified sedimentation relationships based on Stokes' and Newton's laws were formulated to incorporate oil-particle characteristics into the analysis of hydrocarbon behaviour in water. The findings demonstrate that temperature significantly influences the estimated biokinetic parameters and the mathematical description of TPH degradation in freshwater. The study provides a modelling framework for understanding hydrocarbon degradation behaviour and supporting the engineering assessment of petroleum-contaminated aquatic environments. However, further experimental validation is necessary to establish the biological significance of the unusually high-temperature kinetic estimates and verify the consistency of the reported parameters.

Keywords: biokinetics; freshwater environment; temperature effect; total petroleum hydrocarbons; Monod equation; Lineweaver–Burk plot; sedimentation; petroleum pollution

1 Introduction

Petroleum hydrocarbon contamination of aquatic environments is a major environmental engineering concern because of the persistence, toxicity, and ecological effects associated with petroleum-derived organic compounds. The release of crude oil and other petroleum products into freshwater systems can alter water quality, threaten aquatic organisms, and interfere with the natural functioning of aquatic ecosystems. Total petroleum hydrocarbons (TPH) represent an important group of petroleum-related contaminants whose behaviour and degradation in aquatic environments depend on several physical, chemical, and biological factors [1].

Biodegradation is one of the important natural processes through which petroleum hydrocarbons are transformed into simpler compounds by microorganisms. Hydrocarbon-degrading microorganisms utilize petroleum constituents as sources of carbon and energy under suitable environmental

conditions. The effectiveness of this process depends on factors such as temperature, oxygen availability, nutrient concentration, microbial population, substrate concentration, and the physical characteristics of the contaminated medium. Temperature is particularly important because it influences microbial metabolic activities, enzymatic reactions, substrate availability, and the overall kinetics of biological degradation. [2] established the importance of microbial processes in the environmental degradation of petroleum hydrocarbons and highlighted the influence of environmental conditions on hydrocarbon biodegradation [3].

From an engineering perspective, understanding the relationship between temperature and hydrocarbon degradation is essential for developing reliable mathematical models capable of predicting contaminant behaviour under different operating conditions. Kinetic modelling provides a quantitative approach for describing the rate at which microorganisms utilize and degrade organic substrates. One widely applied model is the Monod equation, originally developed to describe the relationship between microbial growth rate and limiting substrate concentration [4]. The model provides important kinetic parameters, including the maximum specific utilization rate and the substrate saturation constant.

The determination of biokinetic parameters is important in environmental engineering because these parameters provide information about the efficiency and potential limitations of biological treatment systems. The Lineweaver–Burk linearization provides an alternative mathematical approach for estimating kinetic parameters by expressing the reciprocal of degradation velocity as a function of the reciprocal of substrate concentration [5].

Apart from biological degradation, the physical behaviour of petroleum droplets in water is another important consideration in the engineering assessment of hydrocarbon-contaminated freshwater. Oil particles may undergo movement, dispersion, flotation, and separation depending on their diameter, density difference, and the physical properties of the surrounding water. Consequently, sedimentation and particle-motion relationships can provide additional information for understanding the physical transport behaviour of oil particles in aquatic environments [6].

Stokes' law describes the terminal settling velocity of spherical particles under laminar-flow conditions, particularly where viscous forces dominate particle motion. The settling velocity is influenced by particle diameter, density difference between the particle and surrounding fluid, and the dynamic viscosity of the fluid. Newton's particle-motion relationship, on the other hand, considers the balance between gravitational and drag forces and is applicable when inertial effects become significant. These relationships provide useful theoretical foundations for modelling particle movement and evaluating the physical behaviour of dispersed materials in water [7].

In petroleum-contaminated freshwater systems, integrating biological kinetic models with particle-settling relationships can provide a broader engineering framework for examining hydrocarbon behaviour. The Monod model describes the substrate-dependent degradation process, while Stokes' and Newton's relationships provide mathematical descriptions of particle motion under different hydrodynamic conditions [8].

Despite the importance of these processes, the quantitative influence of temperature on the functional biokinetic parameters of TPH degradation requires further investigation. In particular, evaluating the maximum degradation velocity and substrate saturation constant at different temperatures can provide useful information for understanding changes in the kinetic characteristics of hydrocarbon degradation systems [9].

Therefore, this study investigates the temperature-dependent biokinetic functional parameters of TPH degradation in freshwater using the Monod kinetic model and Lineweaver–Burk analysis. The investigation considers temperatures of 15, 30, 45, 60, 75, 90, 105, and 120 °C. It also examines modified mathematical relationships based on Stokes' and Newton's laws to describe the sedimentation behaviour of oil particles in freshwater. The overall objective is to establish a mathematical framework for evaluating temperature-related changes in hydrocarbon degradation kinetics and their implications for environmental engineering applications [10].

2 Methodology

2.1 Experimental procedures

A series of experimental procedures was conducted to accomplish the aims and objectives of the study. Initially, the two batch reactors containing saltwater and freshwater, respectively, were thoroughly agitated to ensure uniform mixing and homogeneity of their contents. Samples were subsequently withdrawn from each reactor for physicochemical characterization, Total Bacterial Count (TBC) determination, and Total Petroleum Hydrocarbon (TPH) analysis.

Table 1. Physicochemical parameters and corresponding analytical methods.

S/N	Parameter	Test Method
1	Total Dissolved Solids (mg/L)	APHA 2510B
2	Electrical Conductivity (µS/cm)	APHA 2510B
3	Temperature (°C)	APHA 4500T
4	pH	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	Total Hardness (mg/L)	APHA 2340C
14	Total Suspended Solids (mg/L)	APHA 2340C

Following the initial characterization, each batch reactor was contaminated with 250 cm^3 of crude oil. Thereafter, samples were collected from six (6) uniformly spaced sampling points within each reactor to determine the initial (week 0) values of the previously identified physicochemical parameters. The same sampling and analytical procedures were systematically repeated at two-week intervals throughout the three-month experimental period to monitor changes in the water quality characteristics.

2.2 Determination of total dissolved solids

Total Dissolved Solids (TDS) represent the combined concentration of dissolved substances, including inorganic salts and other soluble compounds, present in a water sample. For the determination of TDS, freshwater and saltwater samples were collected from their respective experimental reactors. Measured portions of each sample were filtered through standard glass-fibre filters, and the filtrates were transferred into previously weighed evaporating dishes. The samples were subsequently dried in an oven at 180 °C until a constant weight was attained. The TDS concentration was then determined from the increase in the weight of the evaporating dishes after drying, which represents the mass of dissolved solids remaining following water evaporation.

2.3 Determination of electrical conductivity

Electrical conductivity (EC) is the ability of a water-based solution to conduct electric current through the movement of dissolved ions. Its magnitude is primarily influenced by the type of ions present, their concentration, ionic mobility, valence, and the temperature at which the measurement is performed. Conductivity measurements were therefore used to assess the concentration of dissolved ionic substances in the freshwater and saltwater samples.

2.4 Determination of pH

The pH of the water samples was determined using an electrometric method with a calibrated pH meter. Before measurement, the instrument was standardized using an appropriate buffer solution. The electrode was then immersed in the water sample to determine its hydrogen ion activity. The electrometric technique was adopted because it provides reliable measurements even in coloured or turbid water samples.

For each determination, approximately 40–45 mL of the water sample was transferred into a clean glass beaker and thoroughly stirred using a clean glass stirring rod. The beaker was covered with a watch glass and allowed to stand for at least one hour to ensure temperature stabilization. Subsequently, the sample temperature was measured, and the temperature setting of the pH meter was adjusted accordingly. The electrode was immersed in the sample, ensuring adequate contact with the water. The beaker was gently rotated to facilitate uniform contact between the electrode and the sample. Once the pH reading had stabilized, the measured value was recorded for subsequent analysis.

2.5 Monod equation

The rate of TPH degradation is expressed according to Monod equation as follows:

$$R_i\left(C\right) = \frac{U_m C_{TPH}}{K_m + C_{TPH}} \tag{1}$$

where C_{TPH} is the concentration of TPH (ppm), k_{d} is the first-order degradation rate constant (day^{-1}), U_{m} is the maximum rate constant ($\mathrm{mg\ L}^{-1}\ \mathrm{day}^{-1}$) and K_{m} is the Monod constant (ppm or mg/L).

2.6 Rate of sedimentation based on Stokes' law

The settling velocity in this case, was developed based on the concept of Stokes' law, which is expressed as:

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

Removing the proportionality, we obtain as follows:

$$v_s = k_F g D_p^2 \left(\frac{\rho_p - \rho_f}{18\mu} \right) \tag{3}$$

Since the oil volume is measurable, the particle diameter, D_p, was expressed in terms of the oil particle volume. Thus, the oil particle is assumed to be spherical in shape. The volume of a sphere is expressed as:

$$V = \frac{\pi D_p^3}{6} \tag{4}$$

Hence, in terms of particle diameter, equation (4) can be stated as:

$$D_p = \left(\frac{6V}{\pi} \right)^{1/3} \tag{5}$$

Substituting equation (5) into (3) gives:

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

After simplification and substitution of equation (6) into (1), we obtained:

$$R_s = K_F g V^{2/3} \left(\frac{\rho_p - \rho_f}{18\mu} \right) \frac{C_{TSS}}{z} \tag{7}$$

2.7 Rate of sedimentation based on Newton's law

Expressing the settling velocity in terms of Newton's law of particle falling in a fluid, we modified the settling velocity as:

$$v_s \propto \left[g D_p \left(\frac{\rho_p - \rho_f}{\rho_f} \right) \right]^{1/2} \tag{8}$$

Removing the proportionality, we obtain as follows:

$$v_s = k_F^* \left[g D_p \left(\frac{\rho_p - \rho_f}{\rho_f} \right) \right]^{1/2} \tag{9}$$

Unlike Stokes' law, Newton's law gives a particle settling velocity that does not depend on the fluid viscosity. Substituting equation (5) into (9) gives:

$$v_s = k_F^* \left(\frac{6V}{\pi} \right)^{1/6} \left[\left(\frac{\rho_p - \rho_f}{\rho_f} \right) g \right]^{1/2} \tag{10}$$

Again, simplification and substitution of equation (10) into (1) gives:

$$R_s = K_F^* V^{1/6} \left[\left(\frac{\rho_p - \rho_f}{\rho_f} \right) g \right]^{1/2} \frac{C_{TSS}}{z} \tag{11}$$

where R_s is the particle settling rate (mg L^{-1} day^{-1}), C_{TPH} is the TPH concentration (mg/L), v_s is the settling velocity (m/s), z is the height of the sample point from the water surface (m), V is the volume of oil (m^3), D_p is the oil particle diameter (m), ρ_p is the oil particle density (kg/m^3), ρ_f is the fluid density (kg/m^3), μ is the viscosity of the fluid (kg m^{-1} s^{-1}), g is the acceleration due to gravity (m/s^2), and K_F and K_F^* are the constants of the settling velocity of the modified Stokes and Newton equations.

3 Results and discussion

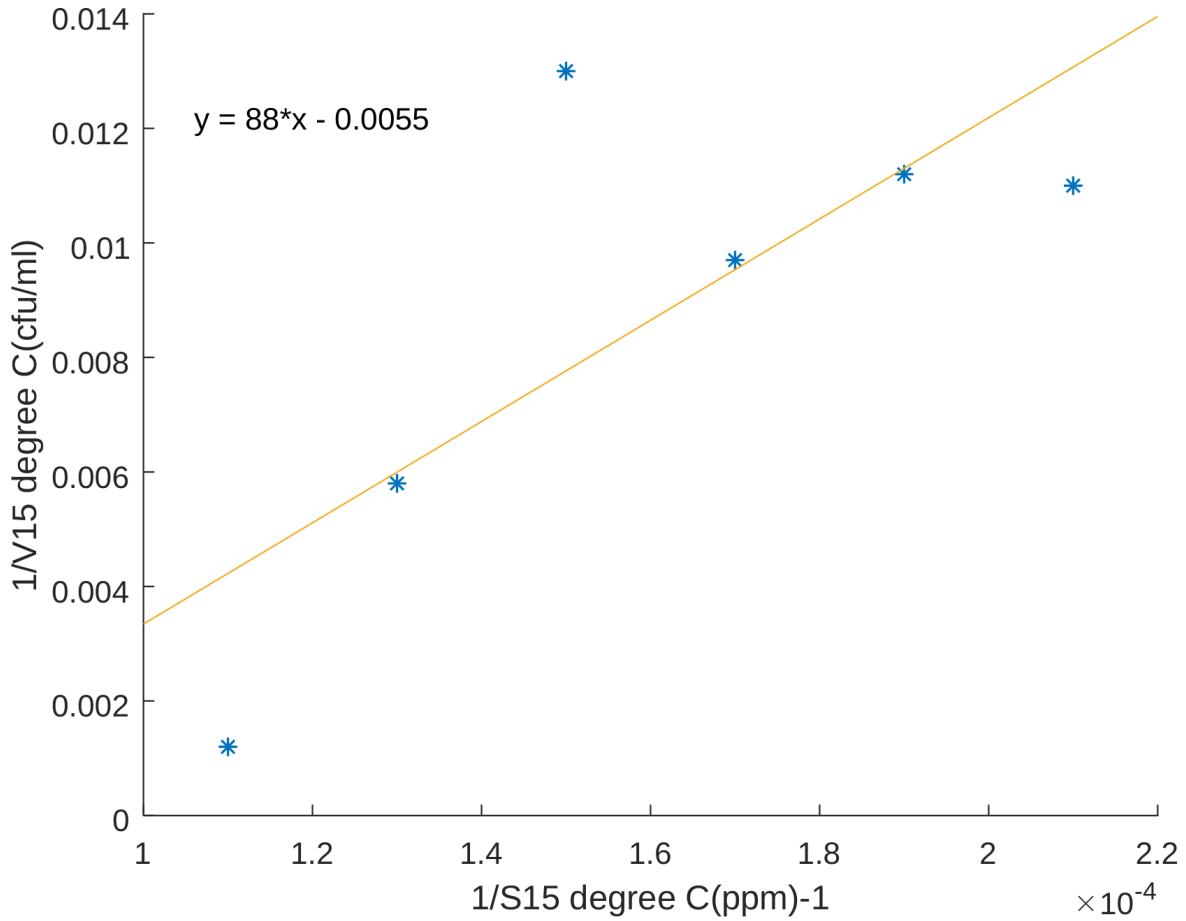


Figure 1. Reciprocal of the velocity (specific rate) of substrate degradation, 1/[V], versus reciprocal of the substrate concentration, 1/[S], at 15 °C.

Figure 1 illustrates the Lineweaver–Burk relationship between the reciprocal of the specific TPH degradation rate (1/V) and the reciprocal of TPH concentration (1/S) in freshwater at 15 °C. The plot initially showed an increase in 1/V with increasing 1/S, followed by a decline. The linear regression equation was y = 88x – 0.0055, with a slope of 88 and an intercept of –0.0055.

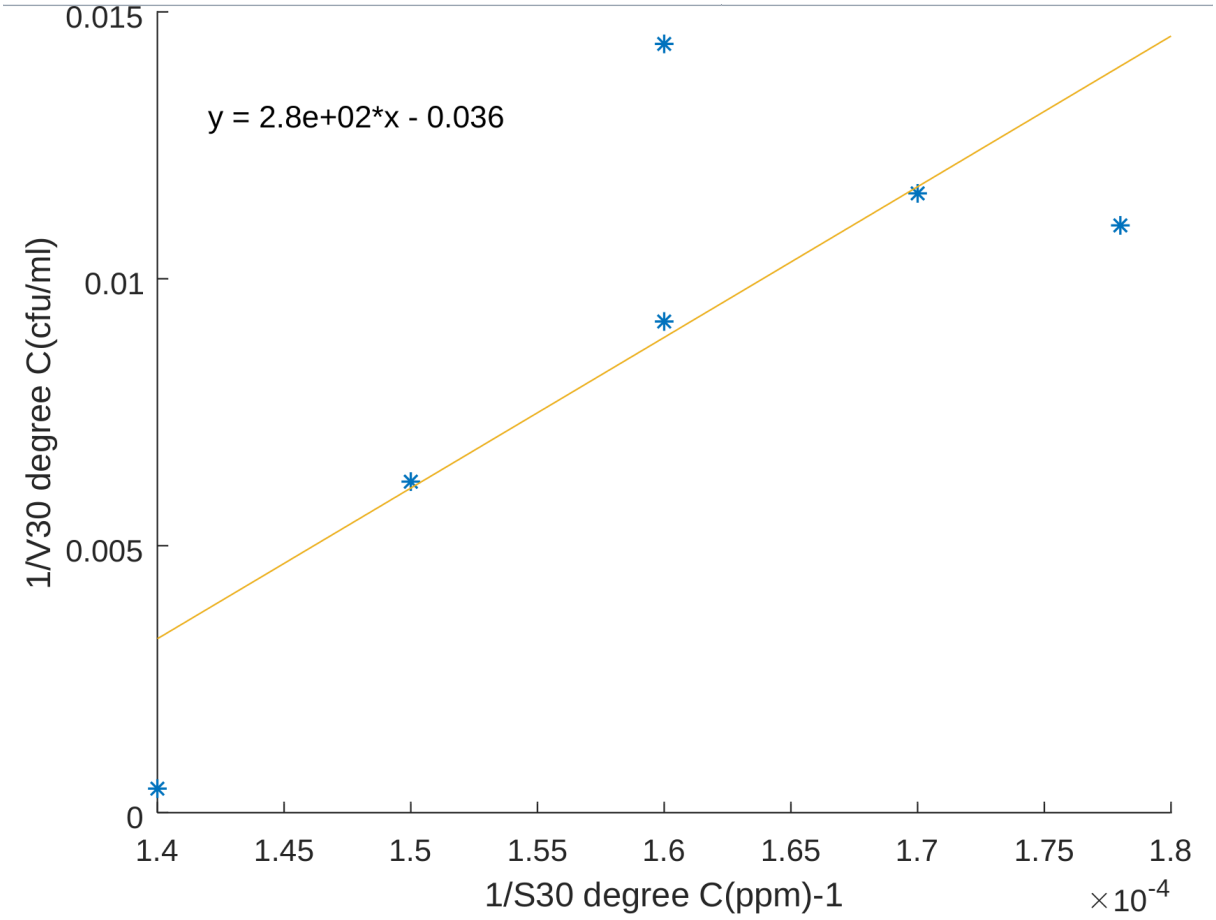


Figure 2. Reciprocal of the velocity (specific rate) of substrate degradation, 1/[V], versus reciprocal of the substrate concentration, 1/[S], at 30 °C.

Figure 2 presents the Lineweaver–Burk relationship between the reciprocal of the specific TPH degradation rate $(1/V)$ and the reciprocal TPH concentration $(1/S)$ in freshwater at 30 °C. The plot initially exhibited an increase in $1/V$ with increasing $1/S$, followed by a decline towards an optimum point. The regression equation was $y = 2.8 \times 10^2 x - 0.036$, with a slope of 2.8×10^2 and an intercept of −0.036. The observed variations in TPH degradation kinetics may be attributed to temperature changes, microbial activity and other environmental factors affecting hydrocarbon biodegradation. At 30 °C the data obeyed the Lineweaver–Burk plot theory; therefore, $V_{\text{max30}} = 333.33\ (\text{ppm/hr})^{-1}$ and $K_{\text{m30}} = 93332\ 40\ (\text{ppm})^{-1}$.

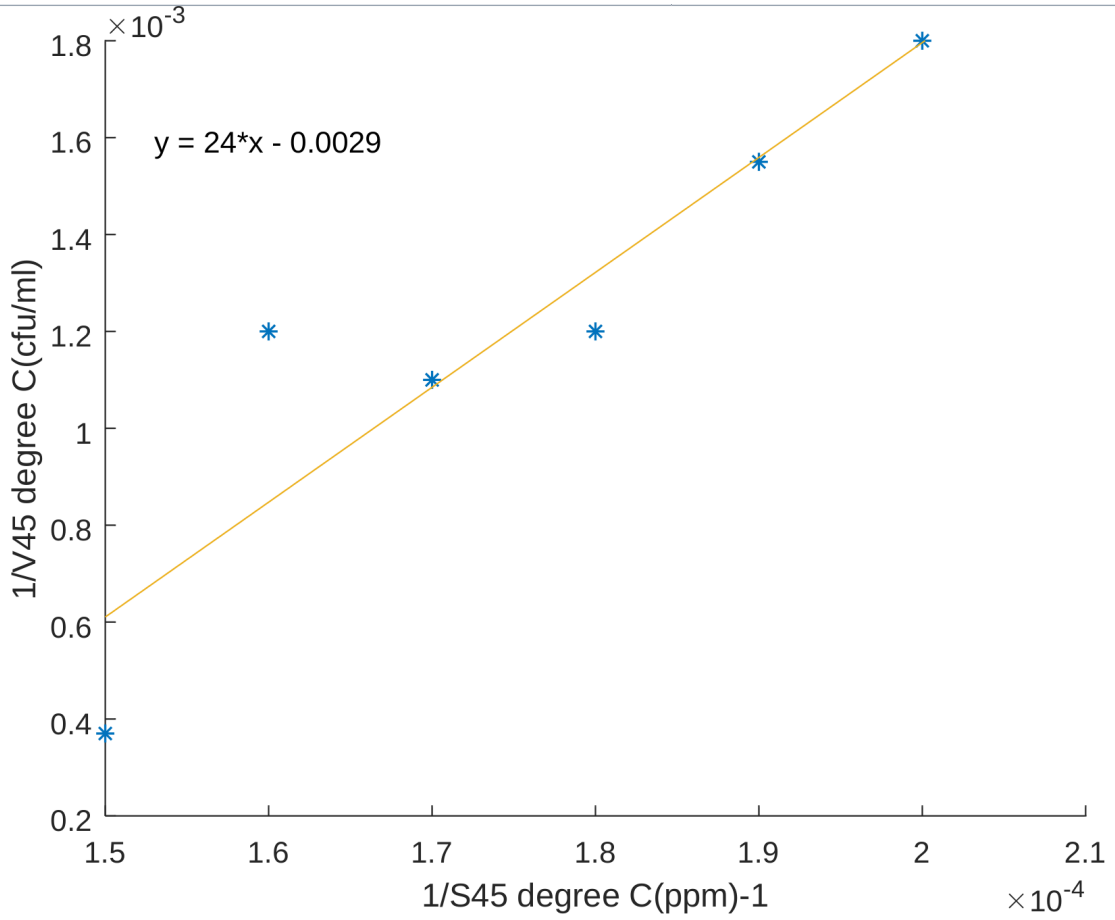


Figure 3. Reciprocal of the velocity (specific rate) of substrate degradation, 1/[V], versus reciprocal of the substrate concentration, 1/[S], at 45 °C.

Figure 3 demonstrates the relationship between the reciprocal of the specific rate of TPH degradation and the reciprocal of TPH concentration at 45 °C. A decrease in the reciprocal of the velocity of TPH degradation was observed with an increase in the reciprocal of TPH (substrate) concentration. The change in the reciprocal of the substrate (TPH) can be traced to the change in the reciprocal of the velocity (specific rate) of TPH (substrate) degradation. The equation of the curve is $y = 24x - 0.0029$, with a slope of 24 and an intercept of −0.0029. The Lineweaver–Burk plot parameters V_{max45} = 1666.67 $(ppm/hr)^{-1}$ and K_{m45} = 40000 $(ppm)^{-1}$ were obtained, as presented in Figure 3.

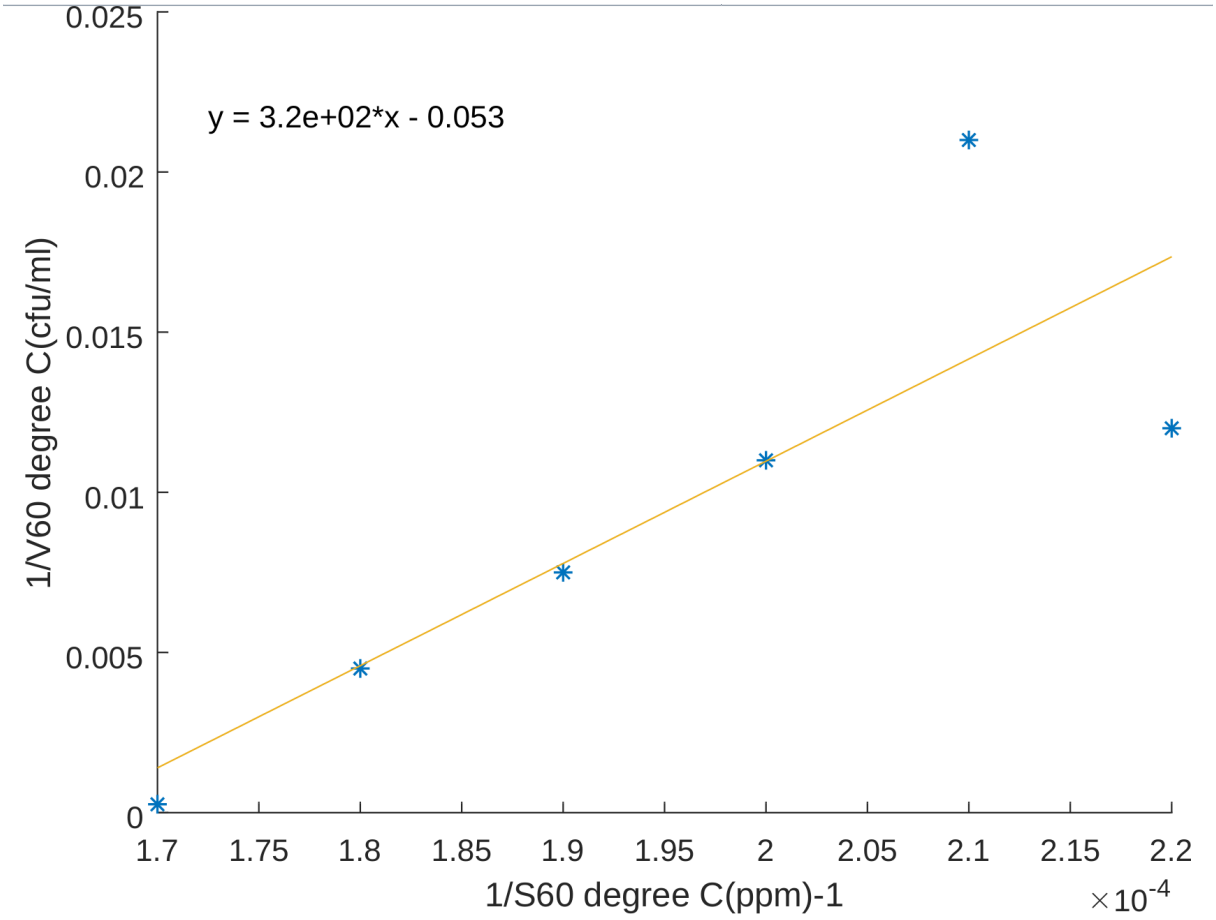


Figure 4. Reciprocal of the velocity (specific rate) of substrate degradation, 1/[V], versus reciprocal of the substrate concentration, 1/[S], at 60 °C.

As seen in Figure 4, the equation of the curve is $y = 3.2 \times 10^2 x - 0.053$, with a slope of 3.2×10^2 and an intercept of −0.053. Therefore, the coefficients of the functional parameters (kinetic values) for the maximum velocity (maximum specific rate) of TPH degradation and the equilibrium or dissociation constant were evaluated as $V_{\max(60\,^\circ\mathrm{C})}$ in $(\mathrm{ppm/hr})^{-1}$ and $K_{s(60\,^\circ\mathrm{C})}$ in $(\mathrm{ppm})^{-1}$.

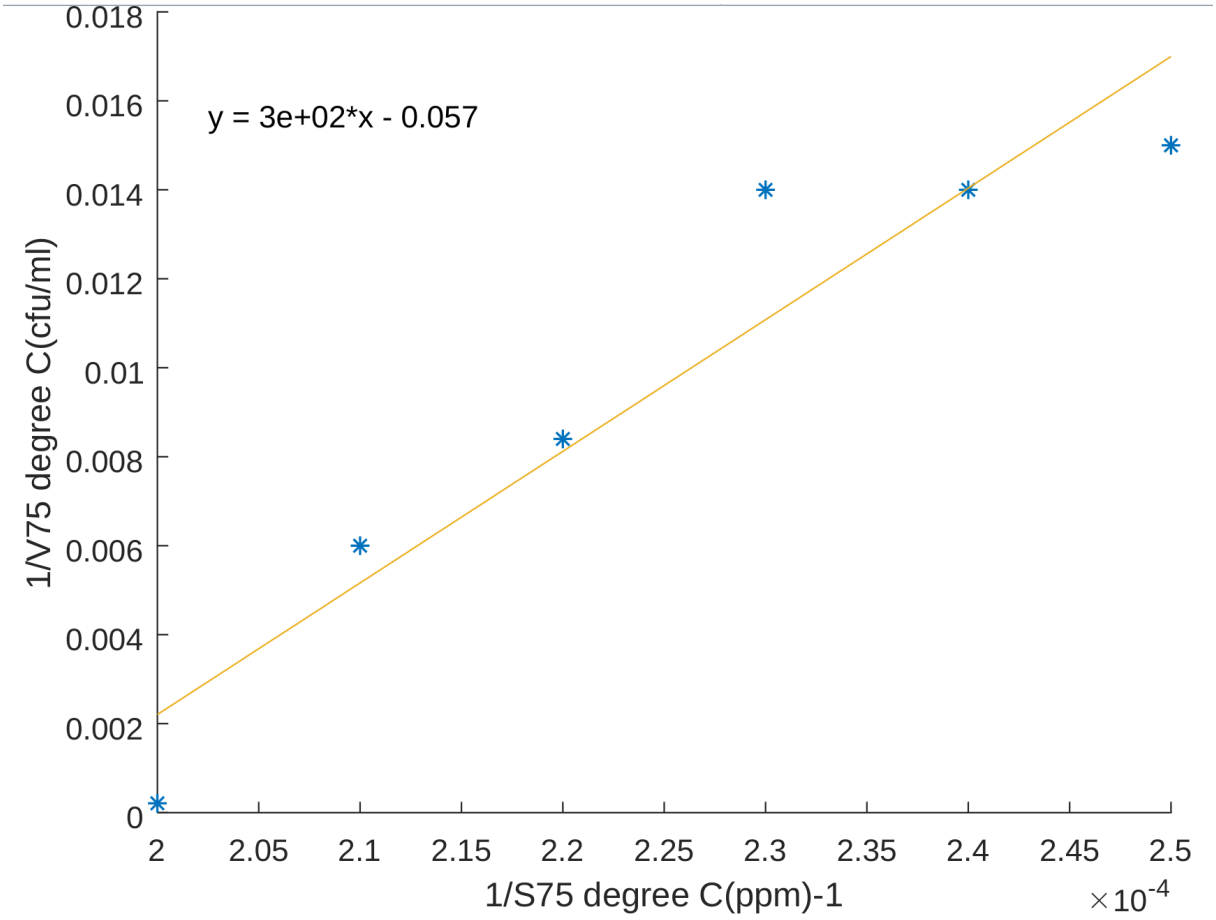


Figure 5. Reciprocal of the velocity (specific rate) of substrate degradation, 1/[V], versus reciprocal of the substrate concentration, 1/[S], at 75 °C.

In Figure 5, a decrease in the reciprocal of the velocity of TPH degradation was observed with an increase in the reciprocal of the TPH concentration, before a sudden increase was noticed. The equation of the curve is $y = 3 \times 10^2 x + 0.057$, with a slope of 3×10^2 and an intercept of 0.057. The change in the reciprocal of the velocity (specific rate) of TPH degradation occurs due to changes in the reciprocal of the TPH (substrate) concentration. The Lineweaver–Burk plot values are V_{max75} = 500 $(ppm/hr)^{-1}$ and K_{s75} = 150000 $(ppm)^{-1}$.

4 Conclusion

This study examined the temperature-dependent biokinetic functional parameters associated with total petroleum hydrocarbon degradation in freshwater using the Monod kinetic model and Lineweaver–Burk analysis. The investigation also incorporated mathematical relationships based on Stokes' and Newton's laws to provide a theoretical understanding of oil-particle sedimentation behaviour in aquatic environments.

The results demonstrated considerable variations in the reported biokinetic parameters across the investigated temperature conditions of 15–75 °C. The estimated maximum degradation velocity and Monod saturation constant exhibited temperature-dependent variations, suggesting that temperature is an important consideration in the mathematical characterization of TPH degradation systems. The regression relationships further demonstrated that changes in substrate concentration were associated with variations in the reciprocal degradation velocity.

The application of the Lineweaver–Burk approach provided a mathematical framework for estimating the maximum degradation velocity and substrate saturation constant from the linear regression relationships. Furthermore, the modified Stokes' and Newton's formulations established theoretical relationships between particle diameter, oil volume, fluid viscosity, density difference, and particle settling velocity. These relationships are useful for examining the physical transport characteristics of petroleum particles in freshwater systems.

The study establishes that mathematical integration of biological kinetic models and particle-motion relationships can provide useful engineering insight into the behaviour of petroleum hydrocarbons in aquatic environments. Such an approach may support the development of predictive models for evaluating hydrocarbon contamination and designing appropriate environmental remediation systems.

However, the reliability of the estimated kinetic parameters requires further verification. In particular, the reported regression intercepts and the corresponding maximum velocity values should be reconciled using the original experimental data. Additionally, experimental investigations should establish the effects of elevated temperatures on microbial viability and actual hydrocarbon degradation.

It is therefore recommended that further investigations incorporate controlled batch-reactor experiments, repeated measurements, appropriate temperature-dependent microbial assessments, and nonlinear regression of the original Monod equation. These improvements would strengthen the accuracy of the kinetic estimates and enhance the applicability of the model to petroleum hydrocarbon biodegradation in freshwater environments.

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