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Performance Evaluation O F A Bioreactor for The Treatment of Produced Water (A Case Study of Crude Oil Dehydration at Kula Flow Station)

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Abstract
Industrial operations such as drilling, chemical manufacturing, petroleum refining, and food processing generate large volumes of effluents containing complex mixtures of organic and inorganic contaminants, including heavy metals, synthetic dyes, hydrocarbons, and toxic compounds. Conventional wastewater treatment systems often struggle to meet discharge standards due to limited efficiency, poor adaptability to fluctuating loads, and high operational costs. This study aims to characterize produced water from a crude oil transportation facility and develop a mathematical model for a continuous stirred-tank bioreactor designed to treat oil- and grease-rich produced water, thereby assessing its performance and stability under varying operating conditions. The model employs a Haldane-Monod kinetic formulation that incorporates substrate inhibition effects and empirical correction factors for salinity and heavy-metal toxicity. Model equations were solved numerically in MATLAB R2020a using the ODE45 solver in conjunction with the Newton–Raphson algorithm to predict substrate and biomass exit concentrations. Process water samples obtained from the Kula facility were characterized for pH, total suspended solids, chemical oxygen demand, biological oxygen demand, and oil and grease, which served as the principal substrate for kinetic evaluation. Simulation results revealed three distinct growth regimes. At substrate concentrations below approximately 10 mgL^{-1}*, microbial growth increased almost linearly with substrate availability, indicating nutrient limitation. Between* $10 - 40mgL^{-1}$*, growth approached a saturation plateau as enzymatically active sites became fully utilized. Beyond 45* mgL^{-1}*, the specific growth rate declined, indicating substrate inhibition, which is commonly associated with inhibitory petrochemical compounds such as phenols, toluene, and xylene. The maximum specific growth rate and endogenous decay constant were determined as* $0.83\ d^{-1}$ *and* $0.05d^{-1}$*, respectively, yielding a maximum permissible dilution rate of approximately* $0.78d^{-1}$*. As the dilution rate increased, substrate concentration initially decreased due to enhanced microbial uptake, while biomass concentration rose correspondingly. At intermediate dilution rates* $0.3 - 0.6d^{-1}$*, the system exhibited a stable operating region characterized by high biomass yield and efficient substrate removal. This plateau zone represents a balance between substrate supply and microbial kinetics, consistent with behaviors reported in MBRs and anaerobic CSTRs treating high-strength wastewater. Beyond this range, further increases in dilution rate led to substrate accumulation and a rapid approach to the washout threshold (>1.0* d^{-1}*), where biomass concentration declined toward zero, and effluent substrate concentration approached the influent value. Oxygen demand increased with dilution rate up to an optimal point before stabilizing, indicating that oxygen utilization is kinetically constrained by microbial activity and substrate availability. Near washout conditions, oxygen demand declined sharply, not from improved efficiency, but from a collapse in microbial population, posing risks of effluent non-compliance.*

Keywords: *Produced water, Bioreactor performance, Oil and gas wastewater, Continuous stirred tank reactor (CSTR), Oil and grease removal, Substrate inhibition kinetics, Mathematical modelling, Wastewater treatment*

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I. INTRODUCTION

Industrialization has been a fundamental driver of global economic progress, enabling large-scale manufacturing, urban development, technological innovation, and improved standards of living. However, these advancements have come at a considerable environmental cost, particularly in the form of increased wastewater generation. Industrial processes from textile dyeing and chemical synthesis to petroleum refining and food processing generate substantial volumes of effluents characterized by a complex mixture of organic and inorganic pollutants, heavy metals, synthetic dyes, hydrocarbons, and toxic chemicals (Kumar *et al.,* 2019). When discharged untreated or inadequately treated, such wastewater can contaminate surface and groundwater

resources, disrupt aquatic ecosystems, and pose significant health hazards to humans and wildlife (Dutta *et al.,* 2021).

The environmental implications of industrial effluents are far-reaching. Pollutants such as heavy metals (e.g., lead, cadmium, mercury), persistent organic compounds, and pathogenic microorganisms can bioaccumulate in aquatic food chains and adversely affect biodiversity (Saxena *et al.,* 2020). In addition, the discharge of oxygen-demanding substances contributes to the depletion of dissolved oxygen in water bodies, leading to eutrophication and the formation of dead zones, which further undermine aquatic life (Garg *et al.,* 2018).

Traditional wastewater treatment methods, including sedimentation, filtration, chlorination, and chemical coagulation often prove inadequate in addressing the complex and variable nature of industrial wastewater streams (Fu & Wang, 2011). These conventional techniques may not effectively remove recalcitrant compounds, and their operational costs, chemical dependencies, and energy intensiveness raise sustainability concerns, particularly in resource-constrained settings.

In light of these challenges, bioreactor technology has emerged as a promising alternative for sustainable wastewater treatment. Bioreactors are engineered systems that utilize microbial consortia to biologically degrade organic and inorganic pollutants in controlled environments. By harnessing microbial metabolism, bioreactors can treat a broad spectrum of contaminants with high efficiency and lower energy requirements compared to conventional systems (Grady *et al.,* 2011). Aerobic and anaerobic bioreactors, including advanced configurations like membrane bioreactors (MBRs), sequencing batch reactors (SBRs), and upflow anaerobic sludge blanket (UASB) reactors, have demonstrated substantial efficacy in treating industrial effluents across diverse sectors (Tchobanoglous *et al.,* 2014).

Moreover, bioreactors offer significant operational flexibility, scalability, and the potential for resource recovery in the form of biogas or reusable treated water. Their environmental benefits, such as reduced greenhouse gas emissions and minimal sludge production in anaerobic systems, make them an environmentally and economically viable solution aligned with circular economy and sustainable development goals (Ali *et al.,* 2020).

Water scarcity remains one of the most pressing global challenges, driven in part by the unsustainable consumption and contamination of freshwater resources by industrial and domestic sectors. A wide array of industries including chemical manufacturing, battery production, metal processing, pulp and paper, textiles, pharmaceuticals, petroleum refining, and power generation consume substantial volumes of water during production processes, subsequently generating large quantities of wastewater laden with harmful pollutants (Ranade & Bhandari, 2014; Shah, 2017). The discharge of untreated or partially treated effluents from these sources contributes significantly to environmental degradation, particularly in aquatic ecosystems.

Industrial wastewater is highly heterogeneous and varies in composition depending on its origin. It typically contains a combination of physical and chemical pollutants. Physical parameters such as total suspended solids (TSS), total dissolved solids (TDS), turbidity, color, odor, and temperature are commonly measured to evaluate water quality. Chemical characteristics are often subdivided into organic and inorganic categories: organic pollutants include biological oxygen demand (BOD) and chemical oxygen demand (COD), which are indicative of the presence of biodegradable and non-biodegradable organics, respectively. Inorganic contaminants encompass parameters such as pH, alkalinity, chlorides, sulfates, and various heavy metals (Swain *et al.,* 2018).

In addition to industrial sources, domestic wastewater generated from urban and rural communities also poses significant pollution risks. Domestic effluents generally consist of human waste (urine and feces), greywater from laundry and kitchen activities, and various household chemicals such as detergents, surfactants, oils, and cleaning agents. Furthermore, agricultural runoff often carries pesticides, herbicides, and fertilizers into water bodies, compounding the pollution load (Mukherjee *et al.,* 2015). The combined impact of these sources underscores the urgent need for effective wastewater treatment strategies to mitigate public health risks and environmental harm.

The generation of large volumes of wastewater from both industrial and domestic sources has become a significant environmental challenge, primarily due to the complex and often recalcitrant nature of the contaminants present in these effluents. Conventional treatment technologies are frequently inadequate for achieving the desired level of purification, particularly in the presence of persistent organic pollutants and high chemical oxygen demand (COD) (Simate & Onyango, 2013). Consequently, the need for efficient and sustainable wastewater treatment strategies has garnered global attention, especially in light of the increasing environmental concerns associated with untreated wastewater discharge (Mandal *et al.,* 2021).

The coffee processing industry is a notable contributor to industrial wastewater, utilizing substantial quantities of water across various production stages. On average, approximately 40–45 liters of wastewater are generated per kilogram of processed coffee, resulting in effluents rich in pollutants such as acidity, offensive odor, coloration, turbidity, high total dissolved solids (TDS), and elevated COD levels (Pujol *et al.,* 2013). Addressing the treatment of coffee wastewater has, therefore, become a subject of interest in numerous studies exploring diverse remediation technologies.

For instance, Zayas *et al.* (2019) reported that a combination of chemical flocculation and advanced oxidation processes achieved up to 87% removal of color, turbidity, and COD from coffee wastewater. Similarly,

Selvamurugan *et al.* (2010) demonstrated that anaerobic and aerobic bioreactor systems were capable of reducing COD by 61% and 68.6%, respectively. In another study, Maike *et al.* (2018) achieved an 87% COD reduction using a continuously aerated bioreactor system. Electrochemical treatment has also shown promise; Sahana *et al.* (2020) employed a batch electrochemical coagulation technique using stainless steel and iron electrodes, resulting in 75% and 91% reductions in COD and color, respectively. Furthermore, Veymar *et al.* (2019) integrated an anaerobic baffled bioreactor with microfiltration for the treatment of wet coffee effluent, achieving reductions of 81% in COD and 61% in TDS.

Wastewater treatment methods are typically categorized into two major classes: physicochemical and biological. Physicochemical methods include processes such as sedimentation, flotation, coagulation-flocculation, ultraviolet (UV) irradiation, and advanced oxidation processes (AOPs) (Teh *et al.,* 2016). These techniques are designed to remove suspended particles, pathogens, and recalcitrant organics based on principles such as gravity settling, hydrophobic interactions, and redox reactions. For instance, sedimentation relies on the density and size of particles to enable settling under gravitational forces, whereas flotation separates hydrophobic contaminants from water through air bubble adhesion.

Biological treatment, on the other hand, utilizes microorganisms to metabolize and degrade organic pollutants. These microbial processes, often aerobic or anaerobic in nature, convert complex organic matter into simpler, less harmful compounds through enzymatically driven pathways. Bioreactors, activated sludge systems, and constructed wetlands are common biological treatment configurations used in municipal and industrial wastewater facilities (Swain *et al.,* 2018).

Advanced oxidation processes (AOPs) represent a hybrid approach that combines chemical and physical methods to achieve high-efficiency degradation of persistent organic pollutants. AOPs typically employ reactive oxidants such as hydroxyl radicals generated through the combination of ozone, UV light, and hydrogen peroxide. These radicals exhibit strong oxidative potential, capable of breaking down aromatic compounds, petroleum hydrocarbons, and volatile organic compounds (VOCs) into non-toxic byproducts (Deng & Zhao, 2015). Despite their effectiveness, the high operational and maintenance costs of AOP systems have limited their widespread application, especially in resource-constrained regions.

1.2 Effluent Water from Oil and Gas Processing Industries

The oil and gas industry is one of the most water-intensive and environmentally impactful sectors globally. During various stages of exploration, drilling, production, refining, and petrochemical processing, vast amounts of water are utilized and subsequently discharged as effluent or produced water. This wastewater, if inadequately treated before disposal or reuse, poses significant environmental and public health risks due to its complex composition and persistent toxicity (Fakhru'l-Razi *et al.,* 2009; Igunnu & Chen, 2014).

1.2.1 Nature and Sources of Effluent in Oil and Gas Operations

The wastewater streams generated in oil and gas operations are broadly categorized based on their source:

- **Produced Water**: This is the largest volume of wastewater in upstream operations. It is a mixture of formation water (naturally occurring underground water), injection water, and residual hydrocarbons brought to the surface during oil and gas extraction (Neff *et al.,* 2011).
- **Process Wastewater**: Generated during refining, cracking, and petrochemical processes, this includes cooling tower blowdown, desalting effluent, sour water, and cleaning waste.
- **Drilling Wastewater**: Contains drilling muds, cuttings, and additives used during drilling and well stimulation.
- **Storm water Runoff**: Collected from open areas of oil and gas installations, potentially carrying oil residues, metals, and sediments.

These effluents differ significantly in composition and toxicity depending on geological conditions, extraction methods, and chemicals used in operations (Jiménez *et al.,* 2018).

1.2.2 Composition and Environmental Hazards

Effluents from oil and gas industries are characterized by a complex mixture of organic and inorganic pollutants, which may include:

- **Hydrocarbons**: Including dispersed and dissolved crude oil, polycyclic aromatic hydrocarbons (PAHs), and volatile organic compounds (VOCs).
- **Heavy Metals**: Such as barium, lead, cadmium, mercury, chromium, and zinc, often originating from geological formations or corrosion inhibitors.
- **Inorganic Salts**: High levels of chloride, sodium, calcium, magnesium, and sulfates are common, especially in produced water, making it highly saline (Al-Ghouti *et al.,* 2019).
- **Radioactive Materials**: Naturally occurring radioactive materials (NORMs), such as radium-226 and radium-228, may be present in formation water and pose radiological hazards.

- **Chemical Additives**: Emulsifiers, corrosion inhibitors, biocides, and scale inhibitors used in enhanced oil recovery can persist in effluents.

The release of untreated effluents into aquatic environments can lead to oxygen depletion, bioaccumulation, toxicity to aquatic organisms, and contamination of groundwater. Chronic exposure to these contaminants can also cause endocrine disruption and carcinogenic effects in humans and wildlife (Boopathy, 2017).

1.2.3 Effluent Standards and Regulatory Framework

Many countries have established regulatory frameworks for managing effluents from oil and gas industries. For instance, the United States Environmental Protection Agency (EPA) under the Clean Water Act has stringent effluent limitation guidelines (ELGs) for offshore and onshore oil and gas operations. Similarly, the Nigerian Department of Petroleum Resources (DPR) mandates maximum permissible limits for oil and grease, BOD, COD, TDS, pH, and other contaminants in produced water before discharge (Nigerian DPR, 2018).

However, compliance with these standards remains a challenge, especially in developing countries where monitoring and enforcement mechanisms are weak. Consequently, untreated or partially treated effluents are often discharged into rivers, wetlands, or used for irrigation, posing long-term environmental threats.

1.2.4 Treatment Technologies for Oil and Gas Wastewater

Given the diverse and complex nature of oil and gas effluents, a combination of physical, chemical, and biological treatment processes is typically required to achieve acceptable discharge or reuse standards.

(a) Physical Treatment Methods

- **Gravity Separation (API Separator)**: Used for removing free oil and suspended solids through sedimentation and flotation.
- **Filtration and Ultrafiltration**: Effective for removing fine particulates and emulsified oil.
- **Membrane Technologies (Reverse Osmosis, Nanofiltration)**: Applied for desalination and removal of dissolved organics and salts, especially in water reuse schemes.

(b) Chemical Treatment Methods

- **Coagulation-Flocculation**: Employs chemicals like alum, ferric chloride, or polymers to aggregate fine particles and emulsions.
- **Advanced Oxidation Processes (AOPs)**: Use of ozone, hydrogen peroxide, or UV to degrade persistent organics like PAHs and surfactants (Deng & Zhao, 2015).
- **Adsorption**: Activated carbon and other porous materials are used for removing volatile organic compounds and hydrocarbons.

(c) Biological Treatment Methods

- **Constructed Wetlands and Bio-filters**: Cost-effective and sustainable methods for removing organics and nutrients in low-strength effluents.
- **Aerobic and Anaerobic Reactors**: Useful for treating sour water and refinery wastewater rich in BOD/COD. However, their performance may be inhibited by salinity, toxicity, and heavy metals (Mohan *et al.,* 2019).

Recently, hybrid systems combining physicochemical and biological processes are being explored to enhance treatment efficiency and address limitations of single-unit operations. For example, coupling membrane bioreactors (MBRs) with reverse osmosis (RO) is proving promising for wastewater reclamation in petrochemical industries (Al-Obaidi *et al.,* 2020).

1.3 Bioreactors used for Wastewater Treatment

Bioreactors are engineered systems designed to support and optimize the biological transformation of substrates into valuable products or by-products through the metabolic activities of microorganisms, enzymes, or cells. They are foundational components in biotechnology, biochemical engineering, and environmental management, offering controlled environments for processes such as fermentation, biodegradation, bioenergy generation, and wastewater treatment (Shuler & Kargi, 2017). The design and operation of bioreactors are governed by principles of mass and energy transfer, reaction kinetics, hydrodynamics, and microbial physiology, making them versatile tools across diverse industrial and environmental applications.

II. MATERIALS AND METHOD

2.1 Materials Used

The materials used for this study includes:

Amber glass bottles, Labels and waterproof markers, PH meter, Dissolved oxygen meter, Filter paper, Analytical balance, Desiccator, Beaker and volumetric flask, Separation funnel, Gas chromatography with flame ionization detector (GC-FID), Oven **Wastewater Characterization**

2.2.1 pH and Temperature Measurement

pH measures the hydrogen ion concentration of a solution and is crucial in determining the corrosiveness, solubility of metals, and chemical equilibrium in wastewater. Temperature influences reaction rates, solubility, microbial activity, and oxygen levels.

Procedure

The probe is immersed directly into the wastewater stream at the discharge point where the effluent exits a treatment system or industrial facility before it enters the environment or is subjected to further processing.

With the probe submerged in the sample, pH is measured immediately. The pH reading indicates the hydrogen ion concentration in the wastewater, representing its acidity or alkalinity. Simultaneously, the probe measures the temperature of the wastewater, typically displayed in degrees Celsius (°C). Temperature affects chemical reaction rates, biological activity, and the solubility of gases like oxygen. Elevated temperatures can indicate industrial discharge, while lower temperatures may slow down biological treatment processes.

Both pH and temperature readings are recorded immediately after stabilization to ensure accurate and representative data.

2.2.2 Total Suspended Solids (TSS)

Total suspended solids (TSS) quantifies particles that are not dissolved in wastewater. These solids can clog treatment systems and increase turbidity, affecting aquatic life.

Procedure

The process begins by measuring a 100mL volume of the wastewater sample. This sample is then passed through a pre-weighed glass fiber filter of pore size 1.5 µm, using a vacuum filtration apparatus. The glass fiber filter is chosen for its high retention efficiency, durability under high temperature, and minimal organic content.

After filtration, the filter retains all the suspended solids present in the sample. To ensure that only the mass of the solids is recorded, the filter is dried in an oven at 105°C for at least one hour or until a constant weight is achieved. This drying temperature is sufficient to evaporate any residual water without decomposing or volatilizing the solid materials.

Once dried, the filter is allowed to cool in a desiccator to prevent moisture uptake from the air, and then it is weighed again. The difference in mass between the initial weight of the dry filter and the final weight after filtration and drying represents the mass of suspended solids captured from the water sample.

This mass difference, expressed in milligrams (mg), is divided by the volume of the water sample filtered (in liters) to calculate the TSS concentration in mg/L:

$$TSS\ \left(\frac{mg}{L}\right) = \frac{weight\ of\ dried\ residue\ (mg)}{Volume\ of\ Sample\ (L)} \quad (1)$$

High TSS values can indicate poor water quality and may interfere with aquatic life, light penetration, and disinfection processes.

2.2.3 Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) is the measure of oxygen required to oxidize organic and inorganic compounds. It is a rapid indictor of pollution strength, especially from petrochemical effluents.

Procedure

a strong oxidizing agent potassium dichromate ($K_2Cr_2O_7$) is introduced to the sample in the presence of concentrated sulfuric acid (H_2SO_4). The acidic medium is essential, as it provides the necessary conditions for the complete oxidation of both biodegradable and non-biodegradable organic compounds. Upon addition, the sample is refluxed with the potassium dichromate-sulfuric acid mixture at 150°C for a period of two hours. This ensures thorough oxidation of the organic content, converting it into carbon dioxide and water, while the dichromate ion ($Cr_2O_7^{2-}$)is reduced to Cr^{3+} in the process.

The oxidation of organic substances containing long-chain aliphatic hydrocarbons can be slow under standard conditions. To enhance the oxidation efficiency, silver sulfate (Ag_2SO_4). is introduced as a catalyst. This catalyst is particularly useful in facilitating the oxidation of straight-chain aliphatic compounds and aromatic hydrocarbons that may otherwise resist oxidation.

After the refluxing process is complete, the amount of unreacted or residual potassium dichromate is quantified to determine how much of it was consumed in oxidizing the organic matter. This is achieved through a back titration technique using ferrous ammonium sulfate (FAS) as the titrant. The Fenton's Advanced System (FAS) reduces the remaining dichromate, and the endpoint of the titration is typically indicated by a color change, often using ferroin as an indicator. The difference between the initial amount of dichromate added and the amount remaining (determined by the titration) directly correlates to the amount that reacted with the organic content in the sample.

The COD value is calculated and expressed in milligrams per liter of oxygen ($mg/L\ O_2$). This value represents the equivalent amount of oxygen that would be required to oxidize the organic material in one liter of the sample, providing a standardized measure of organic pollution. High COD values indicate a high concentration of organic pollutants, suggesting a significant demand for oxygen in the water body receiving the effluent, which can negatively impact aquatic life and ecosystem health.

2.2.4 Biological Oxygen Demand (BOD)

BOD measures the amount of oxygen required by microorganisms to decompose organic matter over five days. It reflects the biodegradable portion of organic pollutants. Specifically, BOD_5 refers to the amount of dissolved oxygen (DO) consumed by aerobic microorganisms over a period of five days at 20°C. This test simulates natural environmental conditions and helps assess the potential impact of wastewater discharge on receiving water bodies.

Procedure

The procedure begins by diluting the wastewater sample with oxygen-saturated water, which serves as a source of dissolved oxygen for microbial activity. This water is prepared by aerating deionized water and adding essential nutrients such as phosphate buffer, magnesium sulfate, calcium chloride, and ferric chloride to support microbial growth. The dilution step is important to ensure that the oxygen demand of the sample does not exceed the amount of available DO during the incubation period. Depending on the expected BOD level, the sample may be diluted in different ratios to maintain measurable oxygen levels at both the start and end of the test.

After preparation, the sample is transferred into airtight BOD bottles, made of glass and designed to prevent gas exchange with the external environment. The initial dissolved oxygen concentration (DO_1) is measured using a calibrated DO meter. This reading represents the amount of oxygen available at the beginning of the test.

The sealed bottles are then placed in a controlled-temperature incubator maintained at 20°C for a period of five days, as recommended by standard testing protocols (e.g., APHA, ASTM, or ISO). During this incubation period, aerobic bacteria in the sample consume the biodegradable organic material, using up oxygen in the process. The microbial metabolism breaks down organic compounds, releasing carbon dioxide and other end products, while reducing the dissolved oxygen concentration.

At the end of the incubation period, the final DO concentration (DO_5) is measured. The difference between the initial and final DO readings indicates the amount of oxygen consumed during the five-day period:

$$BOD_5 = DO_1 - DO_5 \quad (2)$$

The result is expressed in milligrams of oxygen per liter (mg/L). This value provides an estimate of the biodegradable organic load in the water sample. A high BOD_5 value suggests significant levels of organic pollution, which can deplete oxygen in natural waters, leading to adverse effects on aquatic life. Conversely, a low BOD_5 value indicates relatively clean water with little biodegradable material.

2.2.5 Oil and Grease (O&G)

Oil and gas petroleum-derived pollutants such as lubricants and heavy hydrocarbons. High oil and grease concentrations can affect aerobic treatment systems and surface water quality. The method involves extracting non-polar substances such as petroleum hydrocarbons, fats, oils, and waxes from the aqueous phase using a non-polar organic solvent. One of the most commonly used solvents for this purpose is n-hexane**,** owing to its efficiency in dissolving hydrophobic organic compounds and its relatively low boiling point.

Procedure

The process begins with liquid-liquid extraction, in which a measured volume of the water or wastewater sample is transferred to a separatory funnel or extraction vessel. An equal or known excess volume of n-hexane is then added. The sample is thoroughly shaken or mixed to promote contact between the aqueous and organic phases. During this agitation, non-polar compounds such as oils and greases partition into the n-hexane phase, separating them from the water. After mixing, the phases are allowed to settle, and the n-hexane layer containing the extracted oil and grease is carefully collected.

To remove any residual water from the solvent, the hexane extract is dried, by passing it through anhydrous sodium sulfate or another suitable drying agent. This step is crucial to ensure that only oil and grease components are retained in the final measurement and that water does not interfere with the gravimetric analysis.

Following drying, the solvent is subjected to evaporation in a pre-weighed clean evaporation dish or beaker, using a water bath or a hotplate under a fume hood. The n-hexane evaporates, leaving behind the extracted oil and grease residues. Care is taken to avoid overheating, which could cause loss of volatile components or decomposition of the analytes.

The final step is gravimetric measurement, where the dish containing the residual oil and grease is allowed to cool in a desiccator and then weighed using a sensitive balance. The difference in mass between the empty and final dish provides the mass of oil and grease extracted from the sample.

This mass is then used to calculate the oil and grease concentration, usually expressed in milligrams per liter (mg/L):

$$\text{Oil and Grease } \left(\frac{\text{mg}}{\text{L}}\right) = \frac{\text{Mass of residue (mg)}}{volume\ of\ Sample\ (L)} \quad (3)$$

2.2.6 Total Petroleum Hydrocarbons (TPH)

Total Petroleum represents a group of chemical compounds originating from crude oil. It is used to assess the extent of hydrocarbon contamination in industrial effluents. The determination of Total Petroleum Hydrocarbons (TPH) in aqueous samples was conducted using an analytical protocol that combines liquid-liquid extraction with dichloromethane (DCM)**,** followed by instrumental analysis using Gas Chromatography with a Flame Ionization Detector (GC-FID)**.** This method provides a sensitive and selective quantification of hydrocarbon pollutants typically associated with petroleum products, including aliphatic and aromatic hydrocarbons.

Procedure

The first stage of the analysis involved liquid-liquid extraction using dichloromethane (DCM) as the solvent. DCM is a chlorinated organic solvent with strong solvating power for a broad range of hydrocarbon compounds and is commonly used due to its immiscibility with water and ease of evaporation. A 100ml of wastewater sample was transferred into a separatory funnel and extracted with DCM through vigorous shaking. This process promotes the transfer of non-polar hydrocarbons from the aqueous phase into the organic solvent phase.

Following extraction, the DCM layer containing the dissolved hydrocarbons was carefully separated from the aqueous phase and collected. To ensure complete recovery of hydrocarbons, multiple extractions were performed, and the organic layers were combined. The extract was then dried over anhydrous sodium sulfate to remove residual moisture. Subsequently, the solvent was concentrated using a rotary evaporator. This step ensures the hydrocarbons are present at a detectable concentration for the instrumental method.

The concentrated extract was analyzed using Gas Chromatography equipped with a Flame Ionization Detector (GC-FID). In this technique, the sample is injected into a GC system where it is vaporized and carried by an inert gas (usually helium or nitrogen) through a capillary column**.** The column separates the various hydrocarbon compounds based on their boiling points and interactions with the column's stationary phase**.**

As the hydrocarbons elute from the column, they enter the flame ionization detector. In the FID, compounds are burned in a hydrogen-air flame, producing ions. The resulting ion current is measured and is proportional to the quantity of organic compound present. This makes the FID particularly well-suited for detecting and quantifying hydrocarbons due to its high sensitivity to organic carbon.

To quantify the TPH content in the samples, the GC-FID was calibrated using a series of known hydrocarbon standards. These standards, which typically consist of defined mixtures of alkanes (e.g., $C_{10} - C_{40}$), were used to generate a calibration curve correlating the area under each chromatographic peak to the concentration of the hydrocarbon.

During the sample run, each peak on the chromatogram corresponded to a specific hydrocarbon or group of hydrocarbons. The area under the peaks was automatically calculated by the instrument software and compared to the calibration curve to determine the concentration of each component. The total TPH concentration was obtained by summing the concentrations of all relevant peaks within the specified carbon number range (e.g., $C_{10} - C_{28}$).

2.3 Model Development

2.3.1 Kinetics: Monod with Substrate Inhibition and Component Inhibition

Microbial growth with a Haldane/Monod form which accounts for possible substrate inhibition multiplied by multiplicative empirical inhibitor factors for salinity and metals is as shown below:

$$\mu(S,I) = \mu_{max} \frac{S}{K_S + S + \frac{S^2}{K_I}} \times \left(\prod_j \frac{1}{1 + \frac{I_j}{K_{Ij}}} \right) \quad (4)$$

Where;

$\mu(S,I) =$ Specific growth rate under substrate and inhibitor effects

$\mu_{max} =$ Maximum specific growth rate

$S =$ Substrate concentration

$K_S =$ Half-saturation (Monod) constant

$K_I =$ Substrate inhibition constant

$I_j =$ Concentration of inhibitor j

$K_{Ij} =$ Inhibition constant for inhibitor j

Biofilm carriers reduce the effective exposure of cells to inhibitors which is often represented by either (a) increasing effective K_{Ij} for attached biomass or (b) allowing larger SRT and therefore a lower required μ for maintenance (i.e., biofilm effectively raises the community tolerance). In the course of this work, we model this by using two scenarios; conservative and adapted with different K_{Ij} and μ_{max} chosen from halophile literature.

2.3.2 Conservative/Mass Balances for Membrane Bioreactor

in produced water treatment, oil and grease are commonly represented as a lumped hydrocarbon substrate. For modeling purposes, the oil can be approximated by a generic hydrocarbon with empirical formula C_nH_m.

The overall aerobic biological oxidation and growth reaction can be written as:

$$C_nH_m + \left(n + \frac{m}{4} - \frac{1}{2}\right)O_2 \xrightarrow[biomass]{} Y_X C_5H_7NO_2 + (1 - Y_X)\left(nCO_2 + \frac{m}{2}H_2O\right) \quad (5)$$

A simplified form of equation (3.5) is written as;

$$Oil\ \&\ Grease + O_2 \xrightarrow{microorganism} Biomass\ (X) + CO_2 + H_2O \quad (6)$$

This lumped representation of equation (3.6) is suitable for Mono/Haldane kinetic rate law, Yield-based substrate uptake expression and oxygen demand estimation.

In the membrane bioreactor (MBR), oil and grease are removed primarily through aerobic microbial processes involving both oxidation and cellular assimilation. During biodegradation, hydrocarbon substrates are partly incorporated into microbial biomass and partly mineralized to carbon dioxide and water. The coexistence of suspended and attached biomass enhances overall substrate removal efficiency, while biofilm carriers provide protection against inhibitory salts and metals by increasing microbial tolerance and allowing operation at longer effective solid retention times. This configuration supports stable biological treatment of produced water under saline and metal-rich conditions (Judd, 2011; Metcalf & Eddy, 2014; Zhang *et al.,* 2020).

This design is a hybrid Membrane Bioreactor (MBR) with attached biofilm (MBR + carriers/moving-bed media) to treat produced water containing oil and grease (O&G) and inhibitory salts/metals as shown below.

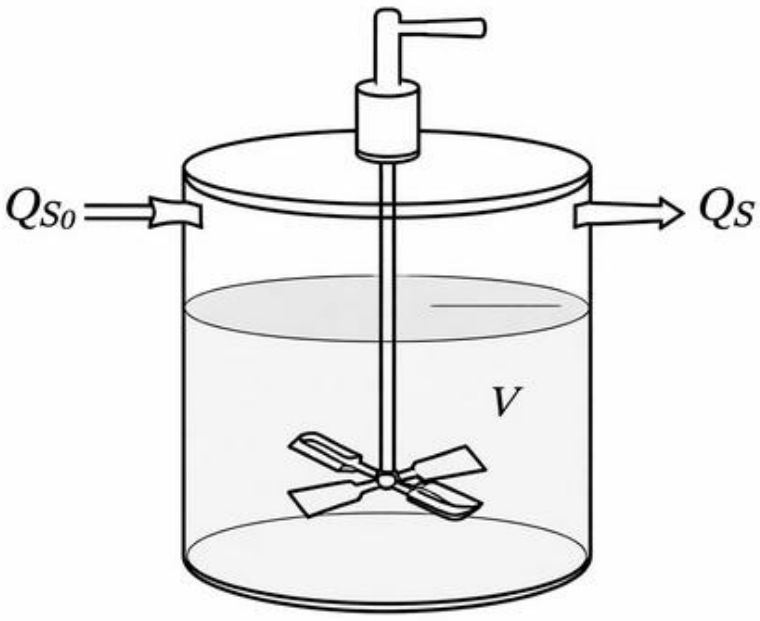

Figure 1: Schematics of a CSTR Bioreactor

The Membrane Bioreactor provides:

- A biofilm habitat that increases biomass retention and inhibitor tolerance and
- Submerged membranes (micro/ultrafiltration) that retain solids and biomass (decoupling Solid retention time from Hydraulic retention time).

This design is based on the principle of conservation of mass which is stated mathematically as:

$$\begin{bmatrix}\text{Rate of inflow of}\\ \text{species A into the}\\ \text{reactor}\end{bmatrix} - \begin{bmatrix}\text{Rate of outflow of species}\\ \text{A out of reactor}\end{bmatrix} - \begin{bmatrix}\text{Rate of depletion of species}\\ \text{A due to chemical reaction}\\ \text{in reactor}\end{bmatrix} = \begin{bmatrix}\text{Rate of Accumulation}\\ \text{of species A in reactor}\end{bmatrix} \quad (7)$$

Substrate (oil and grease) balance in reactor volume, V

$$\begin{bmatrix}\text{Rate of inflow of}\\ \text{species } i \text{ into the}\\ \text{reactor}\end{bmatrix} = QS_0$$

$$\text{Rate of outflow of species } i \text{ out of reactor} = QS$$
$$\text{Rate of depletion of species } i \text{ due to chemical reaction in reactor} = Vr_s$$
$$\text{Rate of Accumulation of species A in reactor} = V\frac{dS}{dt}$$

This is written mathematically as:

$$V\frac{dS}{dt} = QS_0 - QS - Vr_s \quad (8)$$

Where;

S_0 = input substrate concentration (kg/m^3)

S = output substrate concentration (kg/m^3)

Q = Volumetric flow rate $(m^3.s^{-1})$

V = reactor volume (m^3)

r_s = rate of total biological substrate uptake per reactor volume $(mgL^{-1}day^{-1})$.

Equation (3.8) is rearranged to give:

$$\frac{dS}{dt} = D(S_0 - S) - r_s \quad (9)$$

Where;

$$D = \frac{Q}{V} \quad (10)$$

D is defined as the dilution rate with units of day^{-1}. The relationship between dilution rate, D and hydraulic retention time, HRT is given as:

$$HRT = \frac{1}{D} \quad (11)$$

The total substrate uptake r_s from suspended and attached biomass (lumped Monod uptake) is given as:

$$r_s = \frac{1}{Y}(\mu_s(S,I)X_s + \mu_b(S,I)X_b) \quad (12)$$

Assuming the same specific growth function for suspended and attached biomass, $\mu_s = \mu_b$, equation (3.12) simplifies to:

$$r_s = \frac{1}{Y}(\mu(S,I)X) \quad (13)$$

Biomass mass balance

The model represents biological activity using a mixed heterotrophic microbial consortium, which is lumped as the total biomass X. This total biomass comprises both suspended heterotrophic microorganisms (X_s) such as (*Pseudomonas*, *Alcanivorax*) present in the mixed liquor and attached biofilm biomass (X_b) that develops on moving-bed carriers within the membrane bioreactor. The microbial community is predominantly made up of hydrocarbon-degrading, halotolerant and halophilic bacteria that are capable of utilizing oil and grease as their primary sources of carbon and energy, thereby enabling effective biodegradation under saline and inhibitory conditions.

The total biomass mass is given as $M_X = XV$. For total biomass, the dynamic balance is:

$$\frac{d(XV)}{dt} = (\mu - k_d)XV - W \quad (14)$$

Where;

W= biomass wasting $(kg.day^{-1})$ removed to control solid retention time (SRT). Solid retention, θ time is defined as:

$$\theta = \frac{XV}{W} \quad (15)$$

At steady state, equation (3.13) reduces to;

$$\mu(S,I) = k_d + \frac{1}{\theta} \quad (16)$$

Equation (3.16) above is the canonical steady state relation linking growth rate to decay and SRT. Substituting equation (3.16) into (3.9) and setting $\frac{dS}{dt} = 0$ (i.e., steady state) we obtain:

$$D(S_0 - S) = \frac{1}{Y}\left(k_d + \frac{1}{\theta}\right)X \quad (17)$$

Where;

θ = solid retention time

Y = Yield coefficient (biomass produced per substrate consumed)

k_d = Biomass decay (endogenous decay) rate constant

X = Total (lumped) biomass concentration (used when $\mu_s = \mu_b$)

Equation (3.17) shows how microbial activity converts oil and grease into biomass and oxidation products**,** thereby reducing substrate concentration.

Equation (3.17) contains the paired unknown S and X which can be solved numerically because μ depends nonlinearly on S.

Permeate Flux and Membrane area

The membrane area required is given as:

$$A_m = \frac{Q}{J} \quad (18)$$

Where;

$Q =$ Volumetric flow rate $(m^3.s^{-1})$

$A_m =$ membrane area (m^2)

$J =$ membrane flux $(m.h^{-1})$

Oxygen demand and aeration sizing

To estimate oxygen required for biodegradation, removed hydrocarbon mass per day is given by:

$$(S_0 - S_{\text{eff}}) \times Q \quad (19)$$

The expression of equation (3.19) is multiplied by the stoichiometric oxygen demand (O_2 per g hydrocarbon). For a typical aliphatic hydrocarbon, the theoretical O_2 demand is on the order of ~3g O_2 per g hydrocarbon (depends on carbon chain; EPA derivations and biodegradation stoichiometry give 2.5 – 3.5g O_2/g hydrocarbon range). In the course of this work, we use 3.5g O_2/g as a mid-range engineering estimate and refine with fuel composition when available

2.3.4 Model Assumptions

- Steady state Continuous stirred tank reactor configuration integrated with a membrane separation unit.
- Oil and grease (O&G) are the primary target contaminant
- Chloride and dissolved metals are considered inhibitors
- The raw water enters the membrane reactor directly without any pretreatment
- The CSTR is assumed perfectly mixed, with uniform concentration throughout
- Microbial growth rate follows Monod's equation modified for substrate inhibition
- Chloride and heavy metals reduce microbial activity via a multiplicative inhibition factor
- Membrane have near-complete biomass retention (no washout of microorganisms)
- Temperature is maintained at 25^oC
- Sufficient aeration assumed to maintain aerobic conditions

2.3.5 Operating Parameters

Table 1 shows the inlet component concentration of the metallic and nonmetallic pollutants in the waste water as obtained from the laboratory analysis of process water from carried out at Apex Analytics Limited. The complete analysis result is shown in appendix G.

Table 1: Influent Composition of Wastewater

Component	Composition ($mg.L^{-1}$)
Oil and Grease	45.22
Total dissolved solid (TDS)	13500
Chloride	11096.6
Fe	1.896
Zn	0.556
Ba	3.586
Ca	3.792
SO_4^{2-}	22.17
Mg	0.948
Na	8.578

2.3.6 Solution Technique

The mathematical model developed in equation (16) is solved numerically using the Newton – Raphson's method. The Newton – Raphson's method is the most widely used method for the determination of the root of an equation based on accuracy. The newton – Raphson equation can be derived using the Taylor series expansion which is represented partially as:

$$f(x_{i+1}) = f(x_i) + f'(x_i)(x_{i+1} - x_i) + \frac{f''(\aleph)}{2!}(x_{i+1} - x_i)^2 \quad (20)$$

Where $\aleph$ lies somewhere in the interval from x_i to x_{i+1}. An approximate version is obtained by truncating the series after the first derivative term:

$$f(x_{i+1}) \cong f(x_i) + f'(x_i)(x_{i+1} - x_i) \quad (21)$$

At the intersection with the x axis, $f(x_{i+1})$ would be equal to zero, or

$0 = f(x_i) + f'(x_i)(x_{i+1} - x_i)$ (22)

Equation (3.20) above is solved to give

$x_{i+1} = x_i - \frac{f(x_i)}{f'(x_i)}$ (23)

The solution is implemented in MATLAB programming language with the algorithm adapted from as shown in Figure 3.2 and influent composition as shown in Table 1

The following initial and boundary conditions were used:

At $t = 0, S_i = S_{i0}$;

At $t = t, S_i = S_{i(t)}$;

III. RESULTS AND DISCUSSION

3.1 Design Simulation Results

The model equations (8) - (18) was implemented using MATLAB 2020 ODE 45 solver from Matworks using the Newton – Raphson's algorithm in solving the equations in order to ascertain the exit concentration of substrate (S) and biomass concentration (X). The detailed MATLAB program is shown in appendix B - E. The exit values of the various components are as shown in Table 2.

Table 2: Design Simulation Results

Parameter	Value
Substrate conc. (effluent)	0.909mg/L
θ	20.0 days
D	0.781 day^{-1}
S_{opt}	44.7 mgL^{-1}
μ_{peak}	0.83 d^{-1}

3.2: Specific Growth Rate (μ) versus Substrate Concentration (S)

Figure 4.1 presents the relationship between the specific microbial growth rate (μ) and the substrate concentration (S) for the continuous stirred-tank reactor (CSTR) model of the produced water treatment system. The model is based on the Monod expression extended with substrate inhibition as illustrated in equation (3.4), often referred to as the Haldane or Andrews model (Andrews, 1968; Grady *et al.,* 2011).

The curve exhibits three distinct regimes:

Substrate – limited regime (low S)

At substrate concentrations below approximately 10 mgL^{-1}, the growth increases almost linearly with S. this behavior is expected as the microorganisms are nutrient – limited; substrate availability is the controlling factor for growth.

Saturation Regime (moderate S)

Between 10–40 mgL^{-1}, the rate of increase in μ begins to plateau. The microorganisms approach metabolic saturation, where enzyme active sites are nearly fully utilized. Beyond this range, further increases in S only marginally increase the growth rate.

Inhibition regime (high S)

At substrate concentrations above 45 mgL^{-1}, μ begins to decline. This downward trend signifies substrate inhibition, a common phenomenon in process water systems where compounds such as phenols, toluene, and xylene exert inhibitory or even toxic effects at elevated concentrations (Nuhoglu & Yalcin, 2005).

From the model parameters used, the optimum substrate concentration that maximizes the specific growth rate is given by:

$S_{opt} = \sqrt{K_s K_i} = \sqrt{10 \times 200} \approx 44.7\ mgL^{-1}$

At this point the maximum attainable growth rate is approximately:

$\mu_{peak} = \mu(S_{opt}) = \mu_{max} \frac{S_{opt}}{2K_s + S_{opt}} \approx 0.83\ d^{-1}$

This confirms that the optimal operation for microbial activity in the system coincides with an influent substrate concentration near 45 mg mgL^{-1}, which is almost identical to the influent concentration (45.22 mgL^{-1}) assumed in this study.

In continuous systems, microbial growth must balance the dilution rate and decay ($D + K_d$). Since the maximum growth rate observed is 0.83 d^{-1} and the endogenous decay constant is 0.05 d^{-1}, the maximum allowable dilution rate is approximately $D_{max} = 0.78\ d^{-1}$. Operating above this threshold will result in biomass washout, rendering the reactor ineffective.

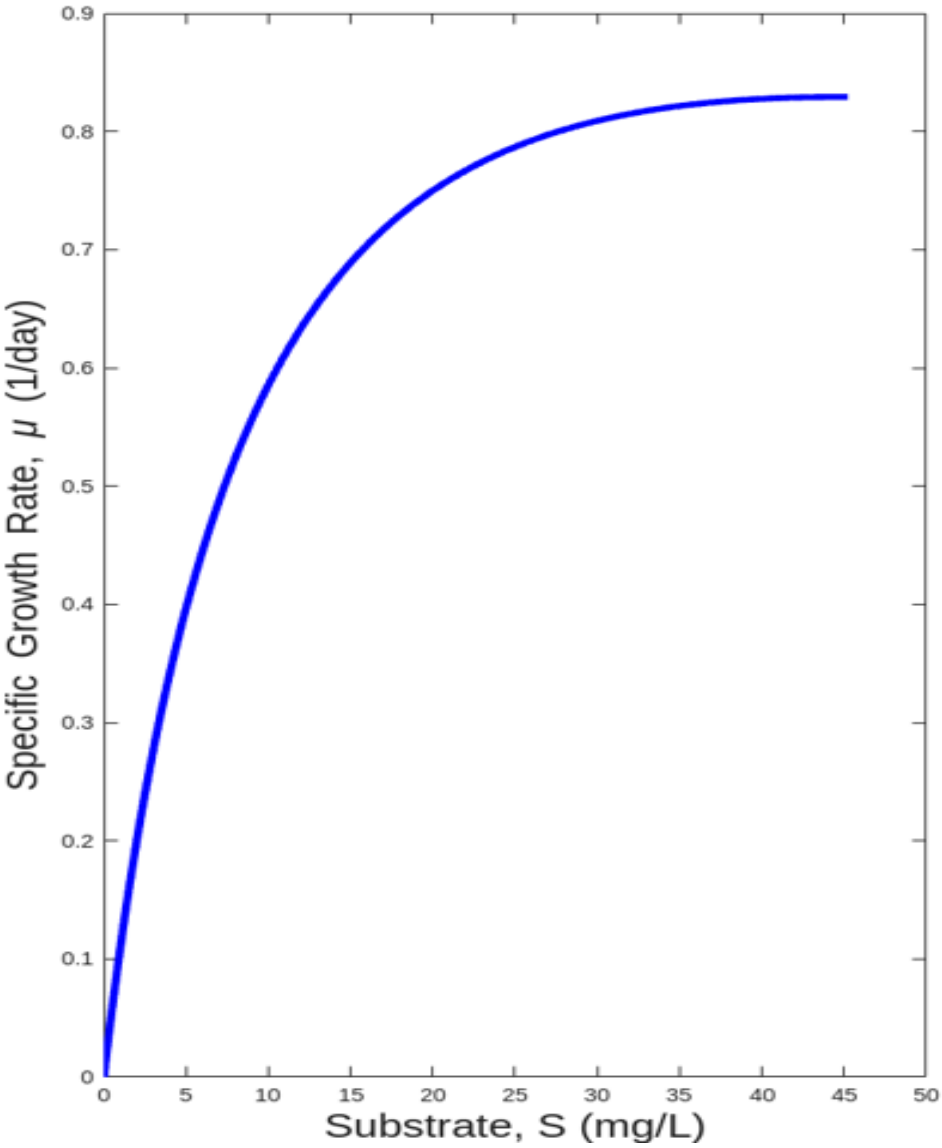

Figure 2: Effect of Substrate concentration on Specific growth rate

IV. CONCLUSION

A mathematical model was successfully developed to describe the substrate and biomass balances in a Continuous Stirred Tank Reactor treating produced water. The model incorporated Monod-type growth kinetics, substrate inhibition, and biomass decay terms to realistically represent the interactions between microbial growth, substrate utilization, and reactor operating conditions. This model formed the foundation for subsequent simulations and performance evaluation.

In this study, the developed mathematical model was successfully simulated using MATLAB with the ODE45 solver, while the Newton–Raphson Algorithm was applied to solve the nonlinear system of equations and determine the exit concentrations of substrate and biomass in the reactor. The simulation results demonstrated that the Continuous Stirred Tank Reactor achieved an effluent substrate concentration of 0.909 mg/L, indicating effective substrate removal and satisfactory treatment performance. The hydraulic retention time of 20.0 days and dilution rate of 0.781 day^{-1} suggest stable reactor operation under the selected design conditions. Furthermore, the optimum substrate concentration of 44.7 mg/L and peak specific growth rate of 0.83 day^{-1} confirmed favorable microbial activity and efficient biodegradation kinetics within the system.

This research contributes to the existing body of knowledge by:

- Formulating a mathematical model for substrate and biomass dynamics in a CSTR treating oil-rich produced water, the study provides a scalable analytical tool that can support reactor design, optimization, and performance evaluation in industrial wastewater treatment applications.

- Analyzing the relationship between substrate concentration and biomass concentration, the work identifies optimal operating zones that maximize microbial activity and treatment efficiency, offering practical guidelines for process control and improved effluent quality.

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