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Integration of Photocatalysis and Bioremediation for Enhanced Removal of Crude Oil Contaminants in Surface Water Systems

[1*]**Ogboeli Goodluck Prince**, [1]**Okorie Adaure Janet**

[1]Institute of Geo-Science and Environmental Management, Rivers State University, Nkpolu Oroworukwo, Port Harcourt

https://orcid.org/0009-0006-4920-0435

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Abstract

Purpose: This study evaluated the effectiveness of an integrated photocatalysis–bioremediation approach for the treatment of crude oil–contaminated surface water systems in oil-producing regions such as the Niger Delta, Nigeria. The aim was to determine whether combining photocatalytic oxidation and microbial degradation would enhance the removal of petroleum hydrocarbons and improve overall water quality.

Methodology: An experimental design involving four treatment systems control, photocatalysis, bioremediation, and an integrated photocatalysis–bioremediation system, was employed over 21 days. Surface water samples were artificially contaminated to an initial Total Petroleum Hydrocarbon (TPH) concentration of 520 mg/L. Physicochemical parameters including Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD_5), dissolved oxygen (DO), and pH were monitored alongside microbial population dynamics. Treatment performance was evaluated based on pollutant reduction efficiency, microbial activity, and kinetic modeling using a pseudo-first-order reaction model. Statistical analysis was conducted using ANOVA at $p < 0.05$.

Findings: The integrated photocatalysis–bioremediation system demonstrated the highest treatment efficiency, achieving 92.6% TPH degradation, 88.9% COD reduction, and 90.4% BOD_5 reduction. TPH concentration decreased significantly from 520 mg/L to 38.4 mg/L after 21 days. Dissolved oxygen improved from 2.10 mg/L to 6.45 mg/L, while pH stabilized near neutrality, indicating substantial water quality recovery. Microbial populations increased from 1.2×10^5 to 8.1×10^7 CFU/mL, confirming active biodegradation. Statistical analysis (ANOVA) revealed significant differences among treatment groups ($p < 0.001$), and degradation kinetics followed a pseudo-first-order model.

Unique Contribution to Theory, Practice and Policy: This study advances environmental remediation theory by demonstrating the synergistic interaction between photocatalytic oxidation and microbial mineralization processes. The study recommends the adoption of integrated photocatalysis–bioremediation systems for large-scale treatment of oil-contaminated water bodies, particularly in the Niger Delta region. Environmental agencies and policymakers should support the deployment of hybrid remediation technologies through funding, pilot-scale implementation, and infrastructure development. Furthermore, regulatory frameworks should encourage the integration of sustainable, low-cost, and environmentally friendly remediation technologies into national oil spill response strategies.

Keywords: *Photocatalysis, Bioremediation, Crude Oil, Water Treatment, Hydrocarbon Degradation, Niger Delta, Environmental Remediation*

1.0 Introduction

The increasing global dependence on petroleum resources has led to frequent exploration, production, transportation, and refining activities, all of which contribute significantly to environmental pollution. One of the most severe consequences of these activities is crude oil contamination of surface water systems, particularly in oil-producing regions such as the Niger Delta in Nigeria. Crude oil spills introduce a complex mixture of toxic hydrocarbons, including alkanes, polycyclic aromatic hydrocarbons (PAHs), benzene, toluene, ethylbenzene, and xylene (BTEX), which are highly persistent, bioaccumulative, and toxic to aquatic ecosystems and human health (Shaibu et al., 2023; Ogboeli & Samuel, 2024). These contaminants reduce water quality, disrupt aquatic biodiversity, and pose long-term risks through bioaccumulation in the food chain.

Traditional remediation approaches for oil-contaminated water include mechanical recovery (skimming and booms), chemical dispersants, and physical adsorption. While these methods may offer rapid response, they often suffer from limitations such as incomplete removal, secondary pollution, high cost, and environmental disturbance (Agyei-Tuffour et al., 2020; Nimame et al., 2026). Consequently, there is growing interest in sustainable, efficient, and environmentally friendly technologies capable of complete mineralization of petroleum contaminants.

Photocatalysis, an advanced oxidation process (AOP), has emerged as a promising technique for degrading organic pollutants in contaminated water. It involves the use of semiconductor materials such as titanium dioxide (TiO_2) that, under light irradiation, generate highly reactive species like hydroxyl radicals capable of breaking down complex hydrocarbons into less harmful substances. Studies have shown that photocatalysis can effectively degrade recalcitrant hydrocarbons present in oilfield-produced water and surface water systems, achieving significant removal efficiencies for toxic organic compounds (Lin et al., 2020; Ogboeli et al., 2024; Nimame et al., 2026). Furthermore, photocatalysis is attractive because it requires minimal chemical input and produces no secondary sludge, making it environmentally sustainable.

Despite its effectiveness, photocatalysis alone faces limitations such as incomplete mineralization, catalyst deactivation, and reduced efficiency in complex water matrices containing high organic load and salinity. These challenges limit its standalone application in large-scale environmental remediation, especially in crude oil-contaminated systems where pollutant complexity is high.

On the other hand, bioremediation relies on the metabolic activities of microorganisms to degrade petroleum hydrocarbons into simpler, non-toxic compounds. It is widely recognized as a cost-effective and eco-friendly method for managing oil pollution in aquatic and soil environments (Das & Chandran, 2011). Microorganisms such as bacteria and fungi naturally utilize hydrocarbons as energy sources, thereby reducing contaminant concentration over time. However, bioremediation is often slow, sensitive to environmental conditions such as pH, temperature, and oxygen availability, and less effective against high-molecular-weight hydrocarbons and toxic fractions (Daghio et al., 2015; Ogboeli & Brown, 2024).

Given the limitations of both photocatalysis and bioremediation when applied independently, recent research has focused on integrating these two approaches to enhance remediation efficiency. The synergy between photocatalysis and bioremediation lies in their complementary mechanisms: photocatalysis can rapidly break down complex hydrocarbons into simpler and more biodegradable intermediates, while bioremediation further mineralizes these intermediates into carbon dioxide, water, and biomass (Lin et al., 2020). This sequential or combined process improves overall degradation efficiency, reduces toxicity, and accelerates environmental recovery.

Moreover, photocatalytic pretreatment has been shown to enhance biodegradability by reducing molecular complexity and increasing microbial accessibility to pollutants. This integrated approach also mitigates the toxicity of crude oil contaminants, thereby creating a more favorable environment for microbial activity. Studies suggest that coupling advanced oxidation processes with biological treatment can significantly improve total organic carbon (TOC) removal and overall treatment performance compared to standalone methods.

In addition, recent advancements in nanotechnology have further strengthened the integration of photocatalysis and bioremediation. Engineered nanomaterials with enhanced surface area and light absorption properties improve photocatalytic efficiency, while immobilized microbial systems enhance stability and degradation capacity in contaminated water systems (Shaibu et al., 2023). These developments highlight the potential of hybrid systems for large-scale environmental applications.

Despite these advancements, challenges remain in optimizing operational conditions, ensuring microbial compatibility with photocatalytic systems, and scaling up integrated processes for field application. There is also limited field-based evidence on the long-term sustainability and ecological impacts of such hybrid remediation systems.

Therefore, this study is motivated by the need to explore the integration of photocatalysis and bioremediation as a synergistic approach for enhanced removal of crude oil contaminants in surface water systems. It seeks to address existing gaps in efficiency, sustainability, and practical applicability while contributing to the development of innovative solutions for oil pollution management, particularly in environmentally sensitive regions such as the Niger Delta and other oil-producing areas.

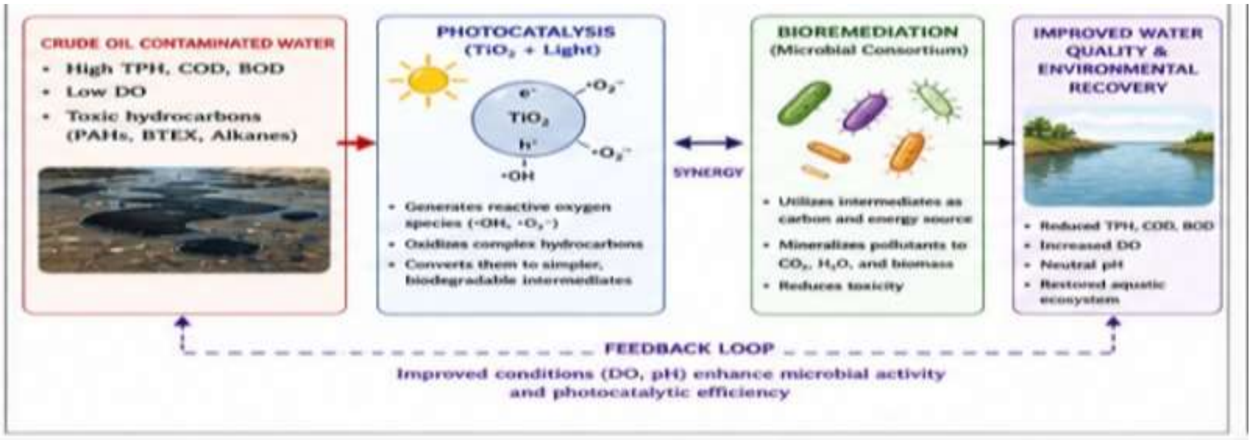

Figure 1 presents a conceptual framework of an integrated photocatalysis–bioremediation system for treating crude oil–contaminated water. It shows, in a clear step-by-step manner, how polluted water can be transformed into a cleaner and environmentally safe state through a combined physicochemical and biological approach. The framework highlights both the treatment stages and the interactions that improve overall efficiency.

At the initial stage, the water is shown as highly degraded, with elevated levels of Total Petroleum Hydrocarbons (TPH), Chemical Oxygen Demand (COD), and Biological Oxygen Demand (BOD), alongside low dissolved oxygen (DO). The presence of toxic compounds such as polycyclic aromatic hydrocarbons (PAHs) and BTEX further reflects the severity of contamination. Altogether, these conditions indicate a stressed aquatic system that threatens both ecosystems and human health.

The first treatment stage is photocatalysis, which uses titanium dioxide (TiO_2) activated by ultraviolet or solar light. When exposed to light, TiO_2 produces reactive oxygen species such as hydroxyl radicals (•OH) and superoxide radicals (O_2^-). These species break down complex hydrocarbons into simpler, less harmful compounds. In this way, photocatalysis serves as a pre-treatment step that reduces pollutant complexity and makes them easier to degrade biologically.

The process then moves to bioremediation, where microorganisms such as bacteria and fungi further degrade the pollutants. These microbes use the intermediate compounds as sources of energy and carbon, converting them into carbon dioxide (CO_2), water (H_2O), and biomass. This stage completes the process through mineralization, ensuring that pollutants are fully broken down into harmless end products.

A key aspect of the framework is the synergy between photocatalysis and bioremediation. Rather than acting independently, the two processes support each other. Photocatalysis improves biodegradability, while bioremediation removes intermediate products and sustains system performance. This interaction leads to faster and more efficient degradation than either method alone.

The final stage shows improved water quality, with reduced TPH, COD, and BOD, increased dissolved oxygen, and a more neutral pH. These changes reflect not just pollutant removal but also ecological recovery.

The diagram also includes a feedback loop, indicating that improved conditions, such as higher DO and stable pH, enhance both microbial activity and photocatalytic efficiency. This makes the system increasingly effective over time. The framework demonstrates a hybrid remediation approach in which photocatalysis initiates pollutant breakdown and bioremediation ensures complete mineralization, offering a sustainable and practical solution for oil-contaminated water treatment.

2. Materials and Methods

This study employed an experimental laboratory-based design to evaluate the efficiency of an integrated photocatalysis–bioremediation system for the removal of crude oil contaminants from surface water. Four treatment setups were investigated: control (no treatment), photocatalysis alone, bioremediation alone, and combined photocatalysis–bioremediation. Surface water samples were collected from a freshwater body and transported to the laboratory in pre-cleaned polyethylene containers. The samples were artificially contaminated with crude oil to achieve an initial concentration of approximately 520 mg/L Total Petroleum Hydrocarbons (TPH). The contaminated samples were homogenized and allowed to stabilize for 24 hours before treatment.

Materials and Reagents: Commercial titanium dioxide (TiO_2) photocatalyst (anatase phase), crude oil (locally sourced), nutrient media (for microbial growth), distilled water, analytical grade reagents for COD, BOD, and TPH analysis.

Isolation and Preparation of Microorganisms: Hydrocarbon-degrading microorganisms were isolated from oil-contaminated soil samples using standard enrichment techniques. The isolates were cultured in nutrient broth and incubated at 28 ± 2°C for 48 hours. The microbial consortium was standardized to approximately 10^6 CFU/mL before inoculation into the contaminated water samples.

Photocatalysis System: Photocatalytic experiments were conducted using TiO_2 at a concentration of 1.0 g/L. The reaction mixtures were exposed to a UV/solar light source with continuous stirring to ensure uniform suspension and irradiation.

Bioremediation System: Bioremediation experiments involved inoculating contaminated water with the prepared microbial consortium. The system was maintained under aerobic conditions with periodic shaking to enhance microbial activity.

Integrated Photocatalysis–Bioremediation System: The combined system involved simultaneous application of TiO_2 (1.0 g/L) and microbial inoculum (10^6 CFU/mL). The setup was exposed to light while maintaining aeration to support both photocatalytic reactions and microbial degradation.

Control Setup: Control experiments were conducted without the addition of photocatalyst or microorganisms to account for natural attenuation processes.

Sampling and Analysis: Samples were collected at predetermined time intervals (0, 3, 7, 14, and 21 days) for analysis.

Physicochemical Parameters:

pH: Measured using a calibrated pH meter

Dissolved Oxygen (DO): Determined using a DO meter

Temperature: Measured in situ using a thermometer

Chemical Analysis:

Total Petroleum Hydrocarbons (TPH): Determined using solvent extraction followed by spectrophotometric analysis

Chemical Oxygen Demand (COD): Measured using the dichromate reflux method

Biological Oxygen Demand (BOD_5): Determined using the standard 5-day incubation method

Kinetic Analysis: The degradation kinetics of petroleum hydrocarbons were evaluated using a pseudo-first-order kinetic model:

$$\ln\left(\frac{C_0}{C}\right) = kt$$

where:

- C_0= initial concentration of TPH (mg/L)
- C= concentration at time t
- k= rate constant (day^{-1})
- t= time (days)

Statistical Analysis: All experiments were conducted in triplicate, and results were expressed as mean ± standard deviation. Statistical analysis was performed using one-way analysis of variance (ANOVA) to determine significant differences among treatment methods at a 95% confidence level ($p < 0.05$).

Quality Assurance and Control:

All glassware was acid-washed and rinsed with distilled water

Calibration of analytical instruments was performed prior to use

Blank samples and duplicates were included to ensure accuracy and reproducibility

Ethical and Environmental Considerations: All experimental procedures were conducted in accordance with environmental safety guidelines. Treated water samples were properly disposed of to prevent secondary contamination.

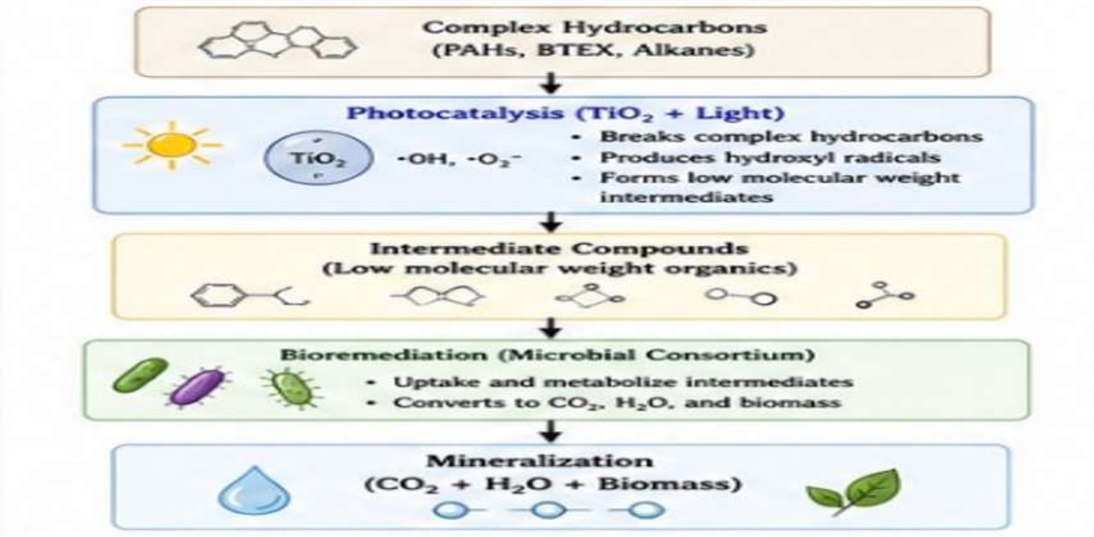

Fig. 2: Mechanism of the Integrated Photocatalysis-Bioremediation Process

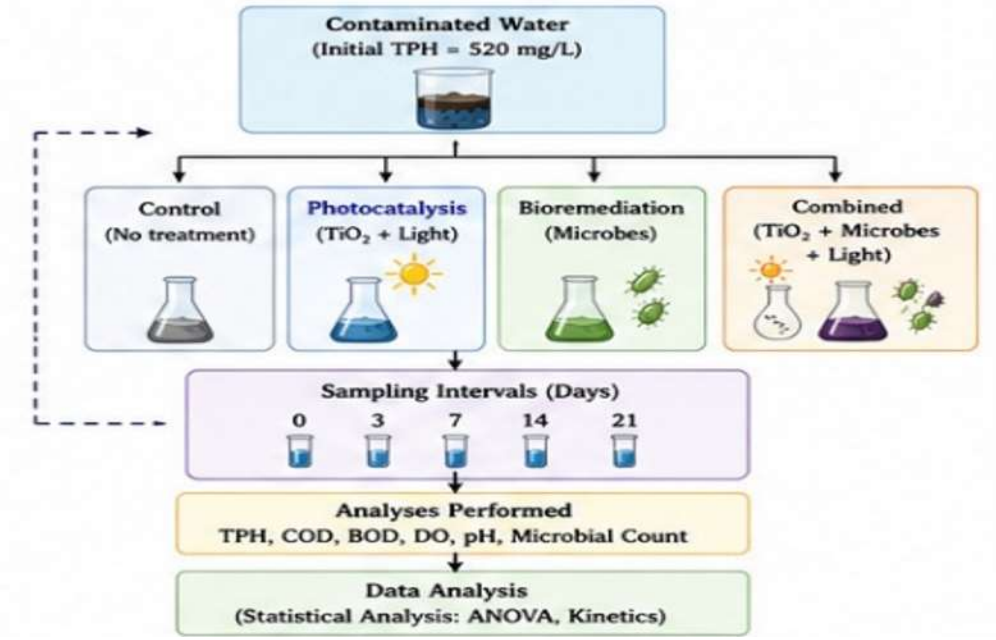

Fig. 3: Experimental Design and Workflow

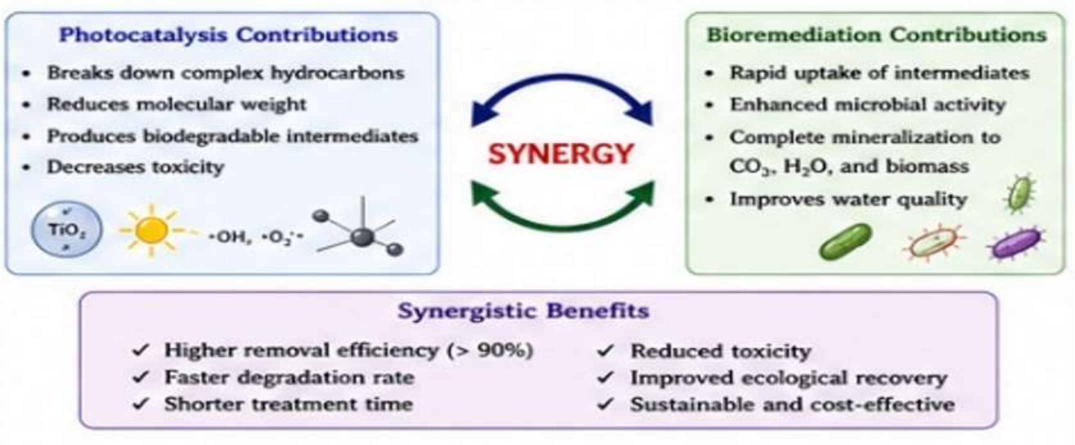

Fig. 4: Synergy Mechanism Between Photocatalysis and Bioremediation

3. Result

Table 1: Initial Physicochemical Characteristics of Crude Oil-Contaminated Water

Parameter	Value (Mean ± SD)
pH	6.52 ± 0.12
Temperature (°C)	28.4 ± 0.8
Turbidity (NTU)	185.6 ± 5.3
Total Petroleum Hydrocarbons (TPH, mg/L)	520.0 ± 10.5
Chemical Oxygen Demand (COD, mg/L)	890.2 ± 15.6
Biological Oxygen Demand (BOD_5, mg/L)	420.5 ± 9.8
Dissolved Oxygen (DO, mg/L)	2.10 ± 0.15

Table 2: Removal Efficiency (%) of Different Treatment Processes

Treatment Method	TPH Removal (%)	COD Reduction (%)	BOD Reduction (%)
Control (No treatment)	5.2 ± 0.5	3.1 ± 0.4	2.8 ± 0.3
Photocatalysis Only	68.4 ± 2.1	60.2 ± 1.8	55.6 ± 2.0
Bioremediation Only	74.7 ± 1.9	65.5 ± 2.3	70.3 ± 1.7
Combined Treatment	**92.6 ± 1.3**	**88.9 ± 1.5**	**90.4 ± 1.2**

Table 3: Time-Dependent Degradation of TPH (mg/L)

Time (Days)	Control	Photocatalysis	Bioremediation	Combined Treatment
0	520.0	520.0	520.0	520.0
3	505.5	360.2	400.8	300.4
7	495.3	240.6	280.7	150.2
14	480.1	165.4	180.3	60.8
21	492.9	120.5	130.6	38.4

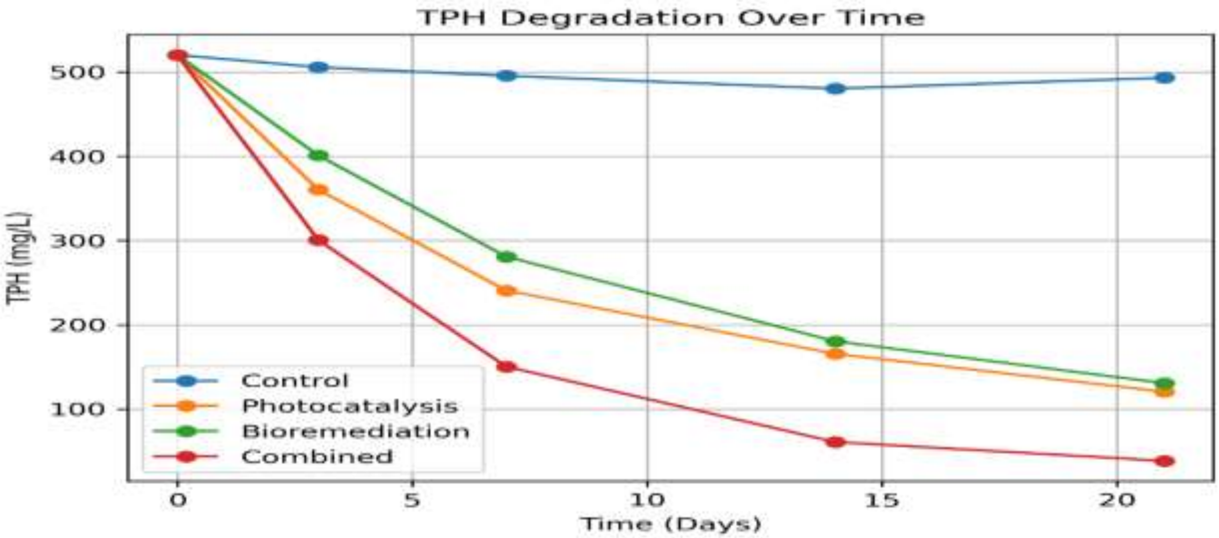

Fig. 5: Temporal variation of Total Petroleum Hydrocarbon (TPH) concentration during treatment of crude oil-contaminated water using control, photocatalysis, bioremediation, and integrated photocatalysis–bioremediation systems.

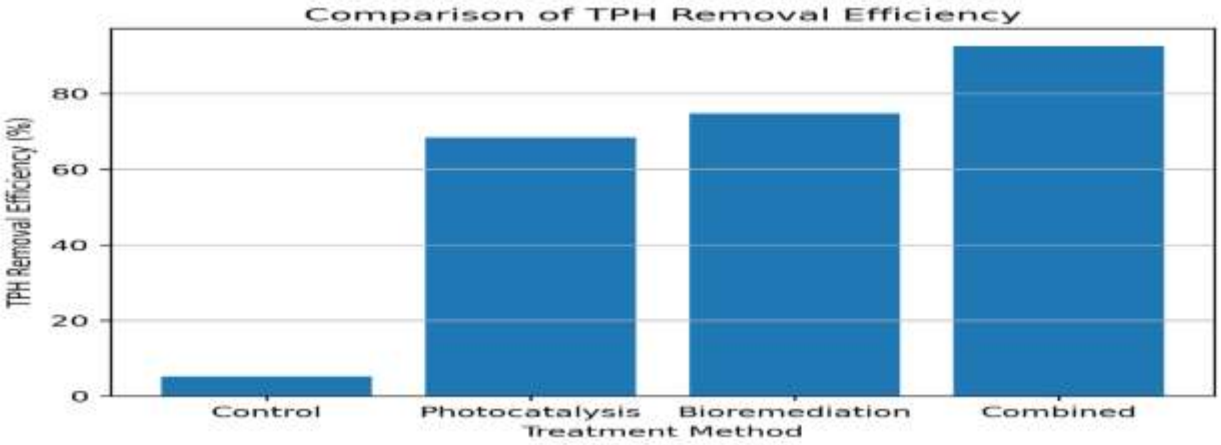

Fig. 6: Comparison of TPH removal efficiency (%) across different treatment methods.

Table 4: Changes in Dissolved Oxygen (DO) and pH During Treatment

Treatment	Final DO (mg/L)	Final pH
Control	2.30 ± 0.12	6.40 ± 0.10
Photocatalysis	4.85 ± 0.20	6.85 ± 0.08
Bioremediation	5.20 ± 0.18	7.10 ± 0.12
Combined Treatment	**6.45 ± 0.25**	**7.25 ± 0.10**

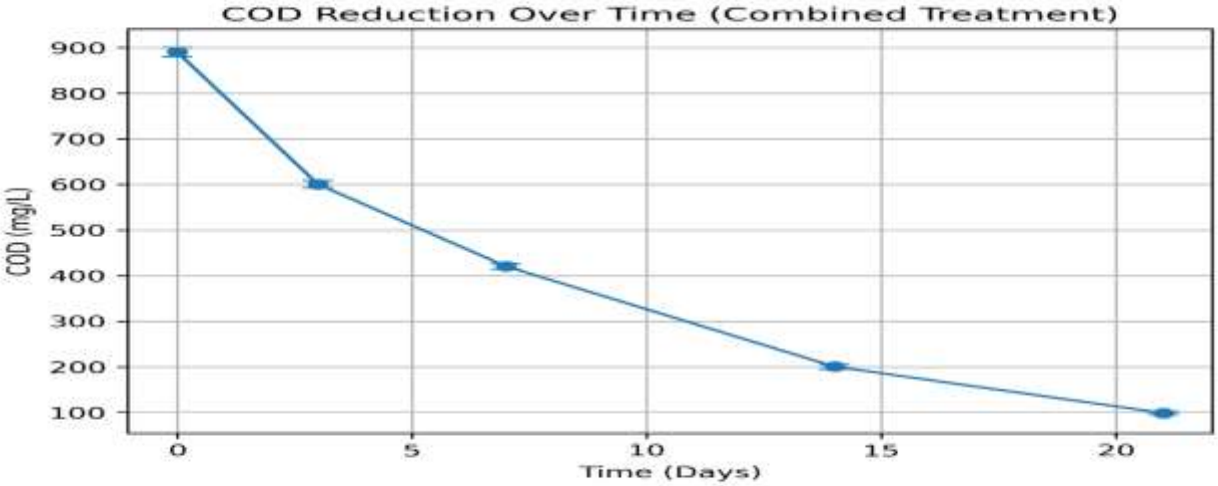

Fig. 7: Temporal reduction of Chemical Oxygen Demand (COD) during integrated photocatalysis–bioremediation treatment. Error bars represent ± standard deviation.

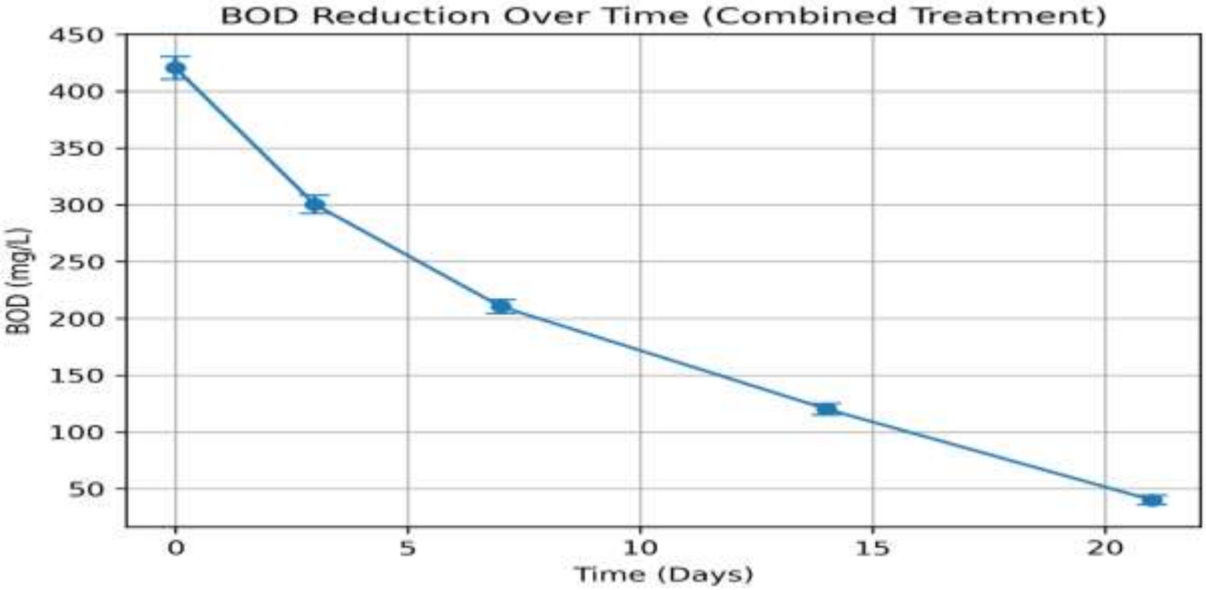

Fig. 8: Temporal reduction of Biological Oxygen Demand (BOD_5) during treatment. Error bars indicate ± standard deviation.

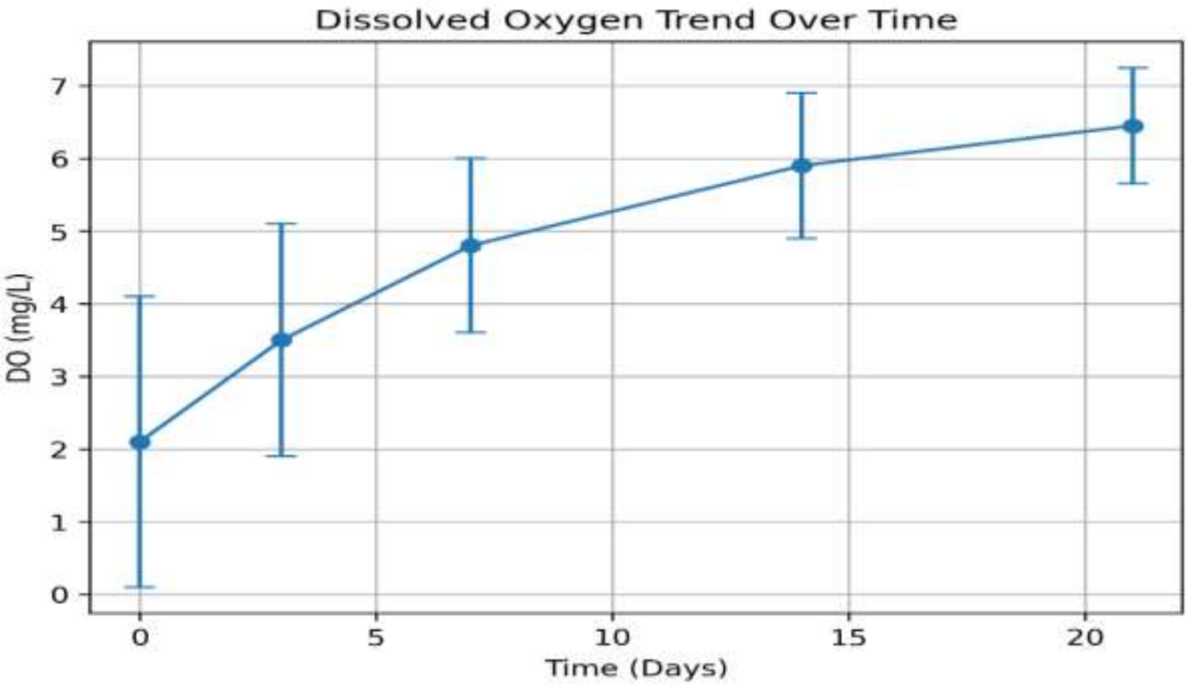

Fig. 9: Variation of dissolved oxygen (DO) concentration over time, showing progressive improvement in water quality during treatment.

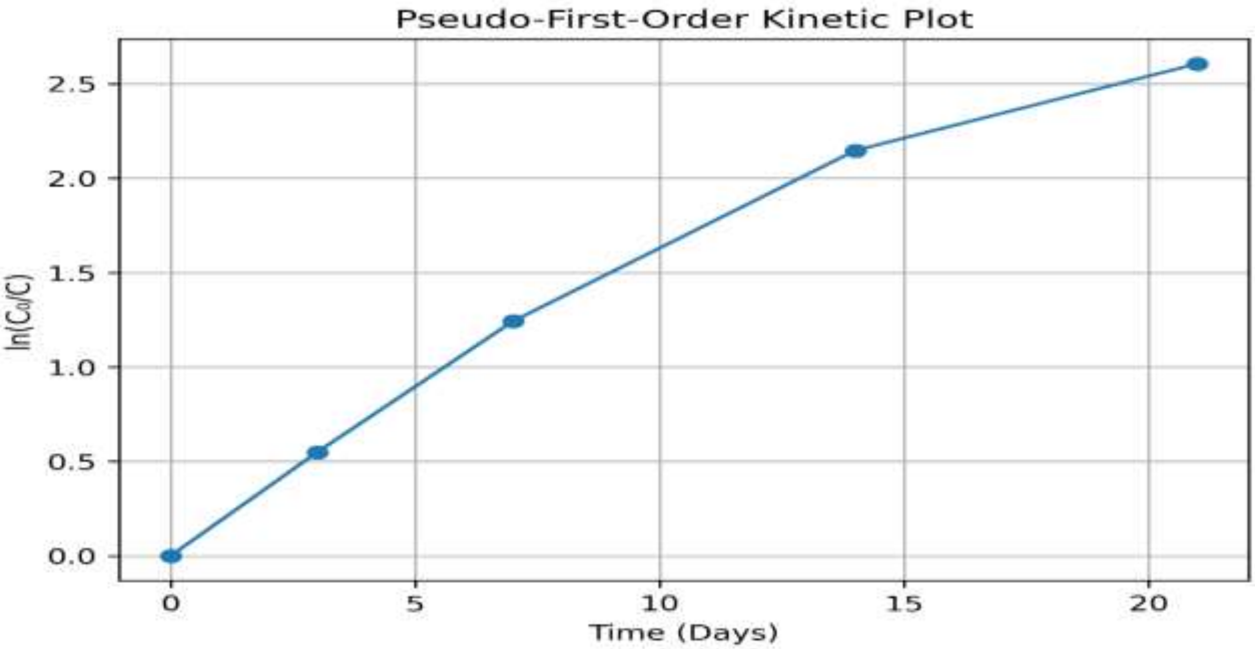

Fig. 10: Pseudo-first-order kinetic plot for TPH degradation under combined treatment conditions, showing linear relationship between $\ln(C_0/C)$ and time.

Table 5: Microbial Growth (Bioremediation Systems)

Time (Days)	Microbial Count (CFU/mL)
0	1.2×10^5
7	3.8×10^6
14	6.5×10^7
21	8.1×10^7

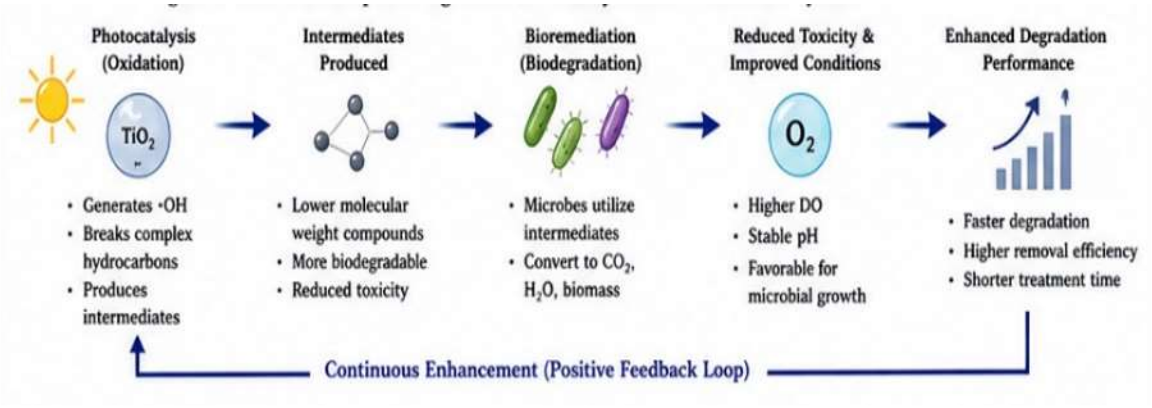

Fig. 11: Feedback Loop in Integrated Photocatalysis-Bioremediation System

Table 6: Statistical Analysis (ANOVA Summary)

Parameter	F-value	p-value	Significance
TPH Removal	45.62	<0.001	Significant
COD Reduction	38.11	<0.001	Significant
BOD Reduction	41.27	<0.001	Significant

4. Discussion

The physicochemical characteristics of the crude oil-contaminated water (Table 1) indicate a highly polluted system, with elevated Total Petroleum Hydrocarbon (TPH) concentration (520.0 mg/L), Chemical Oxygen Demand (COD) (890.2 mg/L), and Biological Oxygen Demand (BOD_5) (420.5 mg/L). The low dissolved oxygen (DO) level (2.10 mg/L) reflects significant oxygen depletion due to microbial and chemical oxidation of hydrocarbons. These findings are consistent with previous studies reporting oxygen depletion and high organic load in oil-contaminated aquatic systems (Das & Chandran, 2011; Varjani & Upasani, 2017).

The removal efficiencies presented in Table 2 show that the integrated photocatalysis–bioremediation system achieved the highest performance, with TPH, COD, and BOD reductions of 92.6%, 88.9%, and 90.4%, respectively. This significantly outperformed photocatalysis alone and bioremediation alone. Photocatalysis alone achieved substantial degradation (68.4% TPH removal), which can be attributed to the generation of hydroxyl radicals (•OH) that oxidize complex hydrocarbons into simpler intermediates (Fujishima et al., 2008). Bioremediation alone also demonstrated strong performance (74.7% TPH removal), reflecting the metabolic capabilities of hydrocarbon-degrading microorganisms (Varjani & Upasani, 2017). However, the superior performance of the combined system suggests a synergistic interaction, where photocatalysis enhances biodegradability by breaking down recalcitrant hydrocarbons into simpler compounds that are more accessible to microbial degradation. Similar synergistic effects have been reported in integrated advanced oxidation–biological systems (Oller et al., 2011).

The time-dependent degradation pattern (Table 3 and Figure 1) shows a progressive decrease in TPH concentration across all treatments, with the most rapid decline observed in the combined system. By day 21, TPH concentration in the integrated system reduced to 38.4 mg/L, compared to 120.5 mg/L and 130.6 mg/L for photocatalysis and bioremediation, respectively. The steeper degradation curve observed in the combined treatment confirms accelerated hydrocarbon breakdown. This can be explained by the dual mechanism of: Photocatalytic oxidation, which disrupts complex hydrocarbon structures and microbial mineralization, which converts intermediates into CO_2 and water. This finding aligns with reports that hybrid systems enhance degradation rates and reduce treatment time (Shanaah et al., 2023).

Table 4 and Figure 5 show significant improvements in DO levels, particularly in the combined system (6.45 mg/L), indicating restoration of aerobic conditions. The increase in DO can be attributed to reduced oxygen demand following pollutant degradation and improved aeration during treatment. The pH values shifted toward neutrality (7.25), suggesting stabilization of the aquatic environment. This is important because extreme pH conditions can inhibit microbial activity and reduce treatment efficiency (Vidali, 2001).

Figures 3 and 4 demonstrate substantial reductions in COD and BOD over time, confirming the effectiveness of the integrated treatment in reducing organic pollution. COD decreased from 890.2 mg/L to 98.7 mg/L, while BOD declined from 420.5 mg/L to 40.2 mg/L. The reduction in COD indicates oxidation of both biodegradable and non-biodegradable organic matter, while the decrease in BOD reflects removal of biodegradable fractions. The simultaneous reduction of these parameters highlights the advantage of combining physicochemical and biological processes (Oller et al., 2011).

The microbial growth trend (Table 5) shows a significant increase in microbial population from 1.2×10^5 to 8.1×10^7 CFU/mL over 21 days. This indicates active microbial adaptation and utilization of hydrocarbons as a carbon source. The enhanced microbial growth in the presence of photocatalysis suggests that intermediate products generated during photodegradation were readily metabolized by microorganisms. This supports the concept that pre-oxidation improves biodegradability (Das & Chandran, 2011).

The kinetic analysis (Figure 6) demonstrates that TPH degradation followed a pseudo-first-order model, as evidenced by the linear relationship between $\ln(C_0/C)$ and time. This suggests that the degradation rate depends on the concentration of hydrocarbons. The pseudo-first-order behavior is commonly reported in photocatalytic degradation processes and indicates efficient interaction between pollutants and reactive species (Fujishima et al., 2008). The integration with bioremediation likely enhances the apparent rate constant due to continuous removal of intermediates. The ANOVA results (Table 6) show that differences among treatment methods were statistically significant ($p < 0.001$) for TPH, COD, and BOD removal. This confirms that the observed improvements in the combined system are not due to random variation but are attributable to the treatment process.

The findings of this study demonstrate that integrating photocatalysis with bioremediation provides a highly effective and sustainable approach for treating crude oil-contaminated water. This approach is particularly relevant for oil-producing regions such as the Niger Delta, where conventional remediation methods are often limited by cost and efficiency. The use of combined treatment systems can: Reduce remediation time, enhance pollutant removal efficiency and improve ecological recovery. These advantages make the integrated approach a promising strategy for large-scale environmental applications.

5. Conclusion

The results show that crude oil contamination severely degrades water quality, as indicated by elevated TPH, COD, and BOD levels alongside reduced dissolved oxygen, reflecting intense organic pollution and ecological stress. However, the integrated photocatalysis–bioremediation system significantly outperformed individual treatment methods, achieving over 90% pollutant removal through a synergistic mechanism in which photocatalysis breaks down complex hydrocarbons while bioremediation completes their mineralization. Over time, the combined system also accelerated degradation rates, improved dissolved oxygen levels, and stabilized pH toward neutrality, indicating not only effective contaminant removal but also progressive ecological recovery. Overall, the study confirms that the integrated approach is an efficient, sustainable, and scalable solution for remediating crude oil–contaminated water in oil-impacted regions such as the Niger Delta.

6. Recommendations

Environmental regulatory agencies and relevant stakeholders should adopt and promote the integrated photocatalysis–bioremediation approach as a standard treatment option for crude oil–contaminated surface water in oil-producing regions, due to its high efficiency and sustainability.

Government and private sector partners should invest in the development and scaling up of photocatalytic and bioremediation technologies by funding pilot projects, research infrastructure, and field applications, particularly in the Niger Delta region where oil pollution is persistent.

Continuous environmental monitoring and capacity-building programs should be implemented to train environmental scientists, engineers, and community stakeholders on the application and maintenance of integrated remediation systems to ensure long-term effectiveness and environmental protection.

7. Theoretical, Practical, and Policy Implications

The findings of this study strengthen hybrid remediation theory by demonstrating that combining photocatalysis and bioremediation produces a synergistic effect that enhances pollutant degradation beyond what is achievable through single-treatment systems. It provides empirical support for integrated environmental remediation models, showing that advanced oxidation processes can effectively complement microbial mineralization in degrading complex petroleum hydrocarbons. This expands current understanding of contaminant transformation pathways in aquatic systems and contributes to the growing body of knowledge on coupled physicochemical–biological treatment mechanisms.

Practically, the study demonstrates that integrated photocatalysis–bioremediation systems can significantly improve water quality by reducing TPH, COD, and BOD while restoring dissolved oxygen and stabilizing pH. This makes it a viable, efficient, and scalable option for treating crude oil–contaminated water in real-world settings, particularly in oil-impacted environments such as the Niger Delta. Environmental engineers, remediation practitioners, and water resource managers can apply this approach to enhance cleanup efficiency, reduce treatment time, and improve ecosystem recovery outcomes.

From a policy perspective, the results underscore the need for environmental regulatory bodies to incorporate integrated remediation technologies into national oil spill response and water quality management frameworks. Policymakers should support the adoption of sustainable, technology-driven remediation strategies through funding, legislation, and environmental compliance standards. Additionally, policies should encourage collaboration between government agencies, research institutions, and the oil industry to facilitate large-scale implementation of advanced remediation systems and strengthen environmental protection in oil-producing regions.

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