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# Experimental study on optimization of chemical oxygen demand reduction through advanced oxidation process for refinery-based oily sludge in Barmer Rajasthan, India

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**Abstract**
This study investigates the optimization of chemical oxygen demand (COD) reduction in oil refinery sludge using advanced oxidation processes (AOPs), addressing the pressing need for effective and sustainable wastewater treatment technologies. AOPs, known for their capacity to degrade complex organic pollutants, are explored under varying operational parameters, including pH, hydrogen peroxide ($H_2O_2$) dosage, ferrous sulfate ($FeSO_4$) concentration, and stirring time. The methodology involves controlled batch experiments to evaluate the individual and combined effects of these parameters on COD reduction efficiency. The study demonstrates that acidic conditions (pH 1.5) and an optimized $H_2O_2$ dosage of 100 ml/L achieves a maximum COD reduction of 57%. Stirring time is found to significantly influence the treatment process, with 90 minutes of stirring under optimal conditions yielding the best results. The inclusion of $FeSO_4$ as a catalyst provides limited enhancement, highlighting the need for further exploration of its role. The research identifies diminishing returns at higher reagent concentrations, emphasizing the importance of parameter optimization to balance efficacy and cost. The study is perhaps the first one of its kinds carried out in the western Rajasthan where a new petroleum refinery in Barmer district is getting ready for its operation very soon. The findings reveal that AOPs can effectively reduce COD in wastewater when operated under specific conditions, offering a sustainable approach for pollution control. Future work should focus on scaling the process for industrial applications, understanding the by-products formed, and investigating synergistic effects of catalysts to enhance performance. This research contributes to advancing wastewater treatment practices in line with global sustainability goals.

**Keywords:** *Oily sludge, refinery waste, COD reduction, advanced oxidation processes*

## Introduction

The reduction of chemical oxygen demand (COD) in refinery sludge is a critical aspect of wastewater management in the petroleum industry. Various treatment methods have been explored to effectively reduce COD levels, which is essential for minimizing environmental impact and complying with regulatory standards. Biological treatment processes, particularly the activated sludge method, are widely employed for treating petroleum refinery wastewater. This method is favored due to its cost-effectiveness and efficiency in reducing both toxicity and dissolved organic constituents (Knight, 2021; Hayder et al., 2014). However, the presence of toxic compounds in refinery wastewater can inhibit microbial activity, posing challenges to effective treatment (Ajao et al., 2013, Jafarinejad, 2019). To address these challenges, alternative biological systems such as sequencing batch reactors (SBR) have been proposed. SBR technology has shown promise in enhancing the mineralization of complex chemicals found in refinery waste, achieving significant reductions in biochemical oxygen demand (BOD) and phenol concentrations

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(Cui et al., 2023, Jafarinejad, 2019). In addition to biological methods, physicochemical treatments are also employed. Techniques such as coagulation-flocculation and oil-water separation are commonly used as pre-treatment steps to remove suspended solids and oils before biological treatment (Hong-yan et al., 2021, Abbassi & Livingstone, 2019). Recent studies have highlighted the effectiveness of advanced oxidation processes, such as UV/$H_2O_2$, in reducing total organic carbon (TOC) and enhancing the biodegradability of refinery wastewater (Cui et al., 2021, Knight, 2021; Jerez et al., 2023). These methods can significantly improve the overall efficiency of COD reduction by breaking down complex organic compounds into simpler, more biodegradable forms (Bień & Bień, 2022). The Fenton process, a well-established advanced oxidation process (AOP), is widely recognized for its efficacy in reducing chemical oxygen demand (COD) in various types of wastewater, including oil refinery sludge. This process relies on the generation of hydroxyl radicals (OH) through the reaction of hydrogen peroxide ($H_2O_2$) with ferrous iron ($Fe^{2+}$), which can effectively oxidize organic pollutants (Abbasi et al., 2015). The optimization of several parameters, including pH, $FeSO_4$ dosage, $H_2O_2$ concentration, and stirring time, is crucial for maximizing COD reduction(Akintayo et al., 2021). The pH of the solution significantly affects the Fenton reaction's efficiency. Optimal COD removal is typically observed at acidic pH levels, with studies indicating that a pH range of 2.5 to 3.5 as most effective for the Fenton process (Rivas et al., 2001; Tony & Bedri, 2014; Costamagna et al., 2021). For instance, a study demonstrated that maximal COD reduction (91.7%) was achieved at pH 3.5 (Tony & Bedri, 2014; Abbasi et al., 2015). This is attributed to the increased availability of $Fe^{2+}$ ions and the enhanced production of hydroxyl radicals under acidic conditions, which are essential for the degradation of organic compounds (Rivas et al., 2001; Bautista et al., 2008; Emoyan et al., 2008). The dosage of $FeSO_4$ is another critical parameter influencing the Fenton process. An appropriate concentration of ferrous iron is necessary to facilitate the reaction with hydrogen peroxide. Studies have shown that increasing $FeSO_4$ dosage can enhance COD removal, but only up to a certain point, beyond which the efficiency may plateau or even decline due to excess iron leading to scavenging of hydroxyl radicals (Trapido et al., 2009; Viggi et al., 2015; Appia & Ouattra, 2023). For example, optimal $FeSO_4$ concentrations have been reported around 90 mg/L, which significantly improved COD reduction rates (Gasim et al., 2013; Dawczak & Dudziak, 2020). Hydrogen peroxide concentration is pivotal in determining the reaction kinetics and overall efficiency of the Fenton process. Research indicates that there is an optimal concentration of $H_2O_2$ that maximizes COD removal. For instance, an optimal $H_2O_2$ concentration of 10 ml was found to achieve a 62% COD reduction in palm oil mill effluent (Awaluddin et al., 2021). However, excessive $H_2O_2$ can lead to reduced efficiency due to the formation of by-products that do not contribute to the oxidation of organic matter (Wang et al., 2008; Kulić et al., 2018). Therefore, careful optimization of $H_2O_2$ concentration is essential for effective treatment. The duration of stirring during the Fenton reaction also plays a significant role in enhancing the contact between reactants, thereby improving the overall reaction kinetics. Studies have indicated that longer stirring times can lead to higher COD removal rates, with some reports suggesting that optimal treatment times can range from 50 to 150 minutes depending on the specific wastewater characteristics and operational conditions (Dawczak and Dudziak, 2020; Solak, 2023). For instance, a stirring time of 50 minutes was effect-tive in achieving significant COD reductions in textile wastewater (Yin and Wang, 2016; Dawczak and Dudziak, 2020). The Fenton process presents a viable method for the reduction of COD in oil refinery sludge, with its efficiency being significantly influenced by pH, $FeSO_4$ dosage, $H_2O_2$ concentration, and stirring time. Optimizing these parameters is essential for maximizing the degradation of organic pollutants and achieving effective wastewater treatment (Prorot et al., 2008).

## Materials and Methods

### Study area

The study focuses on the Rajasthan block RJ-ON-90/1, situated in Barmer district of Rajasthan, India, spanning an area of 3,111 km². The Barmer district, with Barmer as its headquarters, also includes signify-cant towns such as Balotra, Gudamalani, Nokhda, Baytu, Siwana, Jasol, Chauhtan, Dhorimanna, and Uttarlai. Figure 1a shows the location of study area and Figure 1b illustrates the geographical extent of the crude oil block and its geological formations. This block has played a pivotal role in contributing to India's energy sector, generating revenue of appro-ximately USD 15.1 billion for the national and state

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exchequer as of June 30, 2018. Cumulatively, it has produced over 500 million barrels of crude oil. The block's major hydrocarbon discoveries include the Mangala, Bhagyam, and Aishwariya (MBA) fields, with the Mangala field being recognized as the largest onshore hydrocarbon found in India in the past two decades, discovered in January 2004. Subsequently, the Aishwariya and Bhagyam fields were discovered, and to date, a total of 38 hydrocarbon discoveries have been identified within this block, indicating significant potential for further exploration and production. Despite its economic and energy contributions, operations in the crude oil block face critical environmental challenges, primarily related to the management of hazardous wastes. These include oily sludge, produced water, and other by-products of hydrocarbon extraction and processing. Effective treatment, disposal, and management of these waste streams are essential for ensuring compliance with environmental regulations and minimizing ecological impacts. Addressing these environmental challenges is crucial to achieving sustainable operational practices in the block.

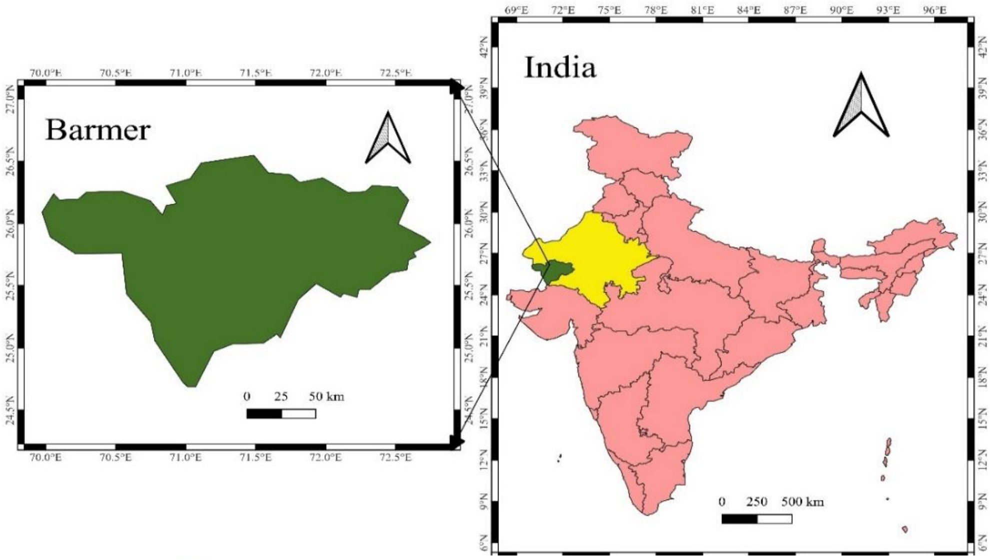


**Figure 1a** *Study area located in Barmer district, Rajasthan India*

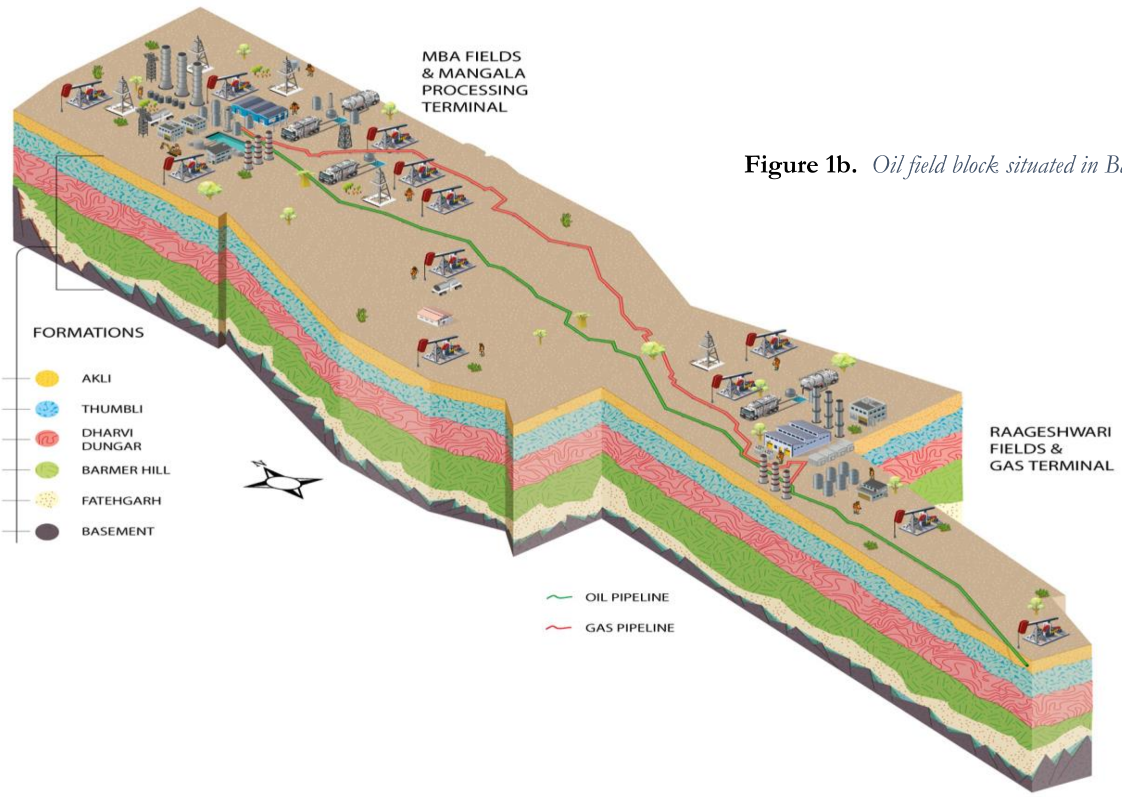


**Figure 1b.** *Oil field block situated in Barmer district*

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**Research methodology**

This study investigates the reduction of chemical oxygen demand (COD) in oily sludge samples collected from the Rajasthan block, specifically from Aishwarya well pad (AWP), Mangla well pad (MWP) and Bhagyam well pad (BWP) as shown in figure 2. Samples were collected on during March 2024 to May 2024 from AWP, MWP and BWP.). The Fenton process was employed for COD reduction, focusing on optimizing key parameters, including pH, $FeSO_4$ dosage, $H_2O_2$ dosage, and stirring time. Initial pH adjustments were performed using sulfuric acid ($H_2SO_4$) and sodium hydroxide (NaOH).Baseline COD levels were measured using the open reflux method as per IS 3025 (Part 58)-2006 (RA 2017).


**Figure 2.** *Locations of sample (oily sludge) collection from AWP, MWP and BWP*

The experimental process began with preparing the oily sludge samples by homogenizing them to ensure uniformity. Pre-measured amounts of sludge were transferred into glass beakers, and the initial COD levels were determined using a COD digester with standard reagents such as potassium dichromate, sulfuric acid, and a ferroin indicator. For each experiment, the pH of the sample was adjusted to the desired level (ranging from 1.5 to 5.5) using $H_2O_4$ and NaOH solution. Next, a calculated dosage of $FeSO_4$ was added, followed by the gradual addition of $H_2O_2$ to initiate the Fenton reaction. The samples were subjected to continuous stirring for a specific time interval (30 to 90 minutes) to ensure proper mixing and reaction. After the reaction, the treated samples were allowed to settle, and the supernatant was collected for COD measurement. COD levels post-treatment were determined using the open reflux method, where samples were digested with potassium dichromate in the presence of concentrated sulfuric acid and a silver sulfate catalyst. The digested samples were titrated with ferrous ammonium sulfate, using ferroin as the indicator to determine COD levels. The percentage COD reduction was calculated by comparing the initial and final COD values. A series of 23 optimization experiments were conducted on Sample 1 to evaluate the impact of varying parameters. The optimal conditions identified were validated on Samples 2 and 3 to ensure consistency and reliability. Experimental data were graphically analyzed to examine the relationships between pH, $FeSO_4$ dosage, $H_2O_2$ dosage, and stirring time during COD reduction. Repeated trials and adherence to standardized procedures ensured the robustness and reproducibility of the findings. This comprehensive experimental methodology demonstrates an effective approach for optimizing the Fenton process to treat oily sludge efficiently.

## Results and Discussion

The physicochemical characteristics of oily sludge play a critical role in determining the selection and efficiency of treatment processes, including Advanced Oxidation Processes (AOPs). Table 1 provides a comprehensive analysis of elemental composition, calorific values, and key physical, chemical, and organic properties of the sludge samples. The above table 1 provides a comprehensive analysis of the chemical, elemental, physical, and thermal properties of three distinct samples (AWP, MWP and BWP). Elemental composition analysis indicates varying concentrations of carbon, hydrogen, nitrogen, sulfur, and oxygen, with Sample 3 showing the highest carbon content (41.1%) and the lowest oxygen percentage (32.77%). Gross and net calorific values reveal significant ener-

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**Table 1.** *The physicochemical characteristics of oily sludge samples*

| Category | Parameter | Unit | Sample 1 (AWP) | Sample 2 (MWP) | Sample 3 (BWP) |
|---|---|---|---|---|---|
| Elemental Composition | Carbon (as C) | % | 19.55 | 15.14 | 41.1 |
| | Hydrogen (as $H_2$) | % | 4.3 | 3.74 | 7.02 |
| | Nitrogen (as N) | % | 0.15 | 0.25 | 0.48 |
| | Sulphur (as S) | % | 1.88 | 1.56 | 2.84 |
| | Oxygen (as $O_2$) | % | 51.49 | 58.33 | 32.77 |
| | Silicon | % | 0.049 | 0.052 | 0.065 |
| | Chlorine | % | 0.43 | 0.65 | 0.24 |
| Calorific Values | Gross Calorific Value | Kcal/kg | 5803.45 | 5791.29 | 2083.35 |
| | Net Calorific Value | Kcal/kg | 5310 | 5240 | 1670 |
| Physical Properties | Density | Kg/L | 0.84 | 0.9 | 0.94 |
| | Viscosity | cSt | 0.056 | 0.045 | 0.06 |
| | pH | - | 6.27 | 7.77 | 6.97 |
| Moisture & Ash | Moisture Content | % | 80.5 | 84.3 | 45.72 |
| | Ash Content | % | 66.24 | 64.21 | 77.74 |
| Inorganic Compounds | Sulphate (as $SO_4$) | mg/Kg | 2.02 | 1.08 | 31.35 |
| | Chloride (as CI) | mg/Kg | 17263 | 1988.64 | 1495.53 |
| | Silicon Dioxide (as $SiO_2$) | mg/Kg | 27.31 | 54.62 | 29.34 |
| | Calcium Carbonate (as $CaCO_3$) | mg/Kg | 3133.8 | 7297 | 34919 |
| | Calcium Oxide (as CaO) | mg/Kg | 2980 | 608.6 | 34919 |
| Metals | Aluminium (as Al) | mg/Kg | 114854.2 | 98147.36 | 1679.63 |
| | Iron (as Fe) | mg/Kg | 24389.58 | 15600.7 | 27834.37 |
| | Calcium (as Ca) | mg/Kg | 5223.56 | 15204.12 | 61185.85 |
| | Zinc (as Zn) | mg/Kg | 73.87 | 103.03 | 71.93 |
| | Nickel (as Ni) | mg/Kg | 19.44 | 19.44 | 95.26 |
| Organics | Total Organic Carbon (as TOC) | mg/Kg | 166.85 | 232.65 | 192 |
| | Total Kjeldahl Nitrogen (TKN) | mg/Kg | 186 | 156.45 | 147 |
| | Total Petroleum Hydrocarbons | mg/Kg | 112.85 | 128.45 | 110 |

gy potential, particularly in Samples 1 and 2, with values exceeding 5000 Kcal/kg. Physical properties, including density and viscosity, exhibit marginal variations across samples, while pH ranges from slightly acidic (6.27) to neutral (7.77). Moisture and ash content are notably high across samples, with Sample 3 presenting a lower moisture content (45.72%) and higher ash content (77.74%). Inorganic compound analysis highlights substantial chloride concentrations, particularly in Sample 1 (17263 mg/Kg), while metal analysis reveals pronounced levels of aluminum, calcium, and iron, especially in Sample 1. The study also evaluates organic parameters such as total organic carbon (TOC) and total petroleum hydrocarbons (TPH), indicating moderate variability across samples. This detailed characterization aids in understanding the physicochemical properties of the samples, providing insights into their suitability for energy recovery, waste management, and/or environmental applications. Table 2 represents experimental details of successive reduction in COD of oily sludge samples. Figures 3a to 3e show variation of pH, $FeSO_4$, $H_2O_2$ and stirring time during experiments conducted on samples 1, 2 and 3 for reduction of COD.The experimental results for the reduction of chemical oxygen demand (COD) in oily sludge highlight the critical role of pH, reagent dosages, and stirring time in determining treatment efficiency. Blank samples were used to establish baseline COD levels. In the initial experiments (Experiments 2–3), the addition of only $H_2O_2$ (100 ml/L) at pH levels of 4.5 and 5.5 led to negative COD reduction percentages, increasing the COD by 10.21% and 27.58%, respectively. This increase is likely due to insufficient oxidation or the

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**Table 2.** *Experimental details of reduction in COD of oily sludge*

| Experiment No. | Sample | Initial COD (Before Dosage) (mg/L) | pH Level | $FeSO_4$ Dosage (g/L) | $H_2O_2$ Dosage (ml/L) | Stirring Time (min) | Final COD (mg/L) | COD Reduction (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | *Blank Sample-01* | 104000 | - | - | - | - | - | - |
| 2 | Sample-01 | 104000 | 4.5 | - | 100 | 90 | 114620 | -10.21 |
| 3 | Sample-01 | 104000 | 5.5 | - | 100 | 90 | 132680 | -27.58 |
| 4 | Sample-01 | 104000 | 1.5 | - | 20 | 45 | 102480 | 1.46 |
| 5 | Sample-01 | 104000 | 1.5 | - | 40 | 45 | 84360 | 18.88 |
| 6 | Sample-01 | 104000 | 2.5 | - | 60 | 90 | 64820 | 37.67 |
| 7 | Sample-01 | 104000 | 1.5 | - | 100 | 90 | 44680 | 57.04 |
| 8 | Sample-01 | 104000 | 2.5 | - | 150 | 90 | 50680 | 51.27 |
| 9 | Sample-01 | 104000 | 1.5 | 1.5 | - | 90 | 101680 | 2.23 |
| 10 | Sample-01 | 104000 | 1.5 | 2.5 | - | 90 | 116820 | -12.33 |
| 11 | Sample-01 | 104000 | 1.5 | 4.5 | - | 90 | 118250 | -13.70 |
| 12 | Sample-01 | 104000 | 1.5 | - | - | 10 | 108620 | -4.44 |
| 13 | Sample-01 | 104000 | 1.5 | - | - | 20 | 102680 | 1.27 |
| 14 | Sample-01 | 104000 | 1.5 | - | - | 40 | 99630 | 4.20 |
| 15 | Sample-01 | 104000 | 1.5 | - | - | 60 | 99340 | 4.48 |
| 16 | Sample-01 | 104000 | 1.5 | - | - | 90 | 99640 | 4.19 |
| 17 | Sample-01 | 104000 | 1.5 | - | 100 | 30 | 86430 | 16.89 |
| 18 | Sample-01 | 104000 | 1.5 | - | 100 | 60 | 78680 | 24.35 |
| 19 | Sample-01 | 104000 | 1.5 | - | 100 | 90 | 72680 | 30.12 |
| 20 | Sample-01 | 104000 | 1.5 | 2.5 | 100 | 90 | 32820 | 68.44 |
| 21 | Sample-01 | 104000 | 3 | 4.0 | 100 | 90 | 26840 | 74.19 |
| 22 | Sample-01 | 104000 | 4 | 6.0 | 100 | 90 | 36740 | 64.67 |
| 23 | *Blank Sample-02* | 119542 | - | - | - | - | - | - |
| 24 | Sample-02 | 119542 | 1.5 | 2.5 | 100 | 90 | 43140 | 63.91 |
| 25 | Sample-02 | 119542 | 2.5 | 4 | 100 | 90 | 32690 | 72.65 |
| 26 | *Blank Sample-03* | 257353 | - | - | - | - | - | - |
| 27 | Sample-03 | 257353 | 1.5 | 2.5 | 100 | 90 | 79665 | 69.04 |
| 28 | Sample-03 | 257353 | 1.5 | 4 | 150 | 90 | 62730 | 75.62 |

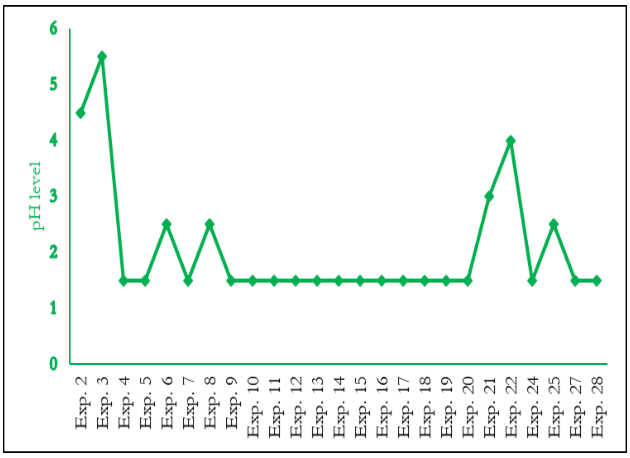


**Figure 3a.** *Variation of pH level during experiments*

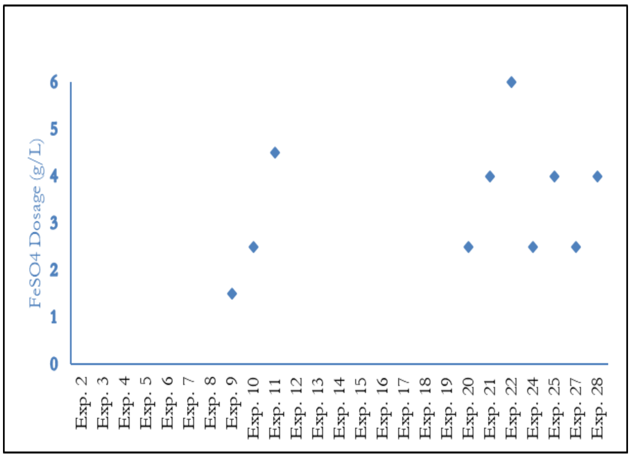


**Figure 3b.** *Variation of $FeSO_4$ dosage during experiments*

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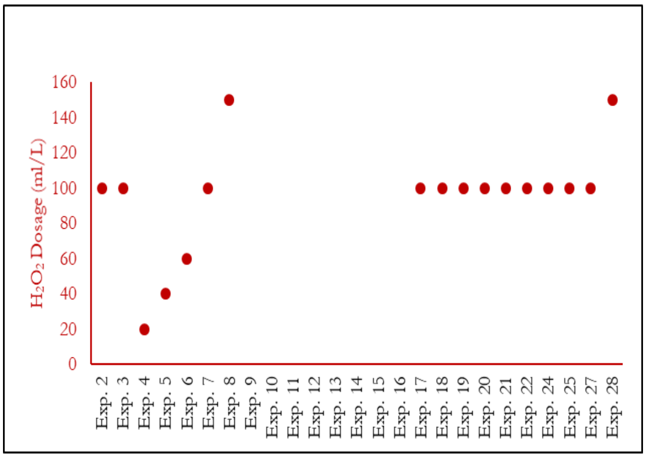


**Figure 3c.** *Variation of $H_2O_2$ dosage during experiments*

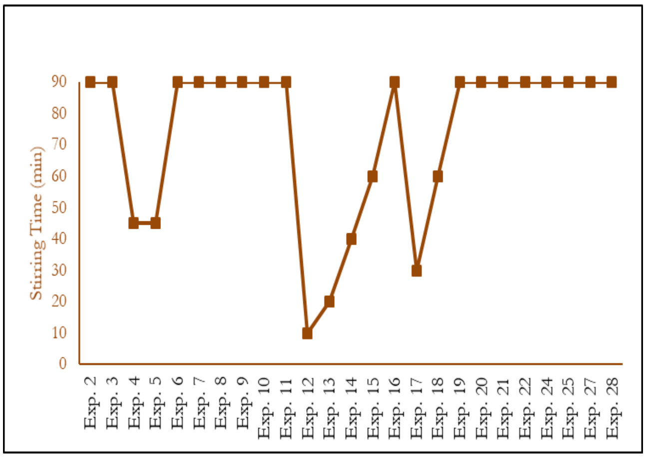


**Figure 3d.** *Variation of stirring time during experiments*

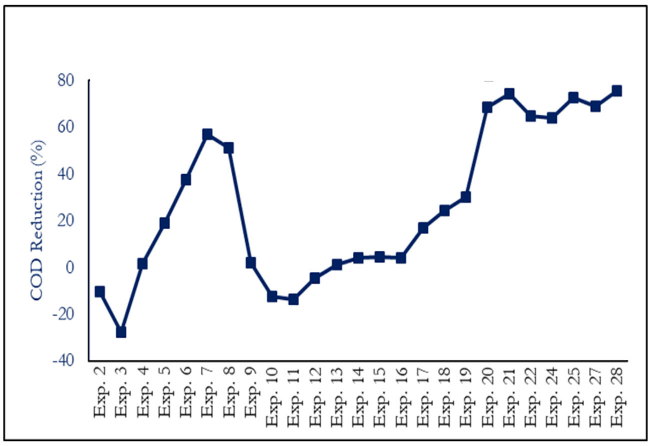


**Figure 3e.** *Variation of COD reduction (%) during experiments*

formation of intermediate organic compounds. Subsequent experiments revealed that adjusting pH to 1.5 and optimizing $H_2O_2$ dosages improved COD reduction, with Experiment 7 achieving a reduction of 57.04% using 100 ml/L $H_2O_2$, pH 1.5, and 90 minutes of stirring as shown in table 2. However, increasing the $H_2O_2$ dosage beyond 100 ml/L (Experiment 8) resulted in diminished efficiency, indicating a threshold beyond which excess oxidant may hinder the process. The inclusion of ferrous sulfate ($FeSO_4$) as a catalyst demonstrated a synergistic effect in COD reduction. Experiments 20 and 21 achieved reductions of 68.44% and 74.19%, respectively, by combining $FeSO_4$ (2.5–3 g/L) with $H_2O_2$ (100 ml/L) at pH levels of 1.5–4.0. These findings underscore the importance of balancing the catalyst and oxidant to maximize treatment efficiency. In contrast, experiments without $H_2O_2$ or with suboptimal $FeSO_4$ dosages (Experiments 9–11) resulted in negative COD reductions, emphasizing the critical role of $H_2O_2$ in oxidative degradation. Additional expe-riments on Sample-02 and Sample-03 further vali-dated the optimized conditions. For Sample-02, COD reductions of 63.91% and 72.65% were achieved with $FeSO_4$ dosages of 2.5 g/L and 4 g/L, respectively, coupled with $H_2O_2$ (100 ml/L). Similarly, Sample-03 exhibited a maximum COD reduction of 75.62% under optimal conditions ($FeSO_4$: 4 g/L, $H_2O_2$: 150 ml/L, pH: 1.5). These results highlight the reprodu-cibility of the optimized parameters across different sludge samples. Overall, the study identified key treatment parameters for effective COD reduction, including an optimal pH range of 1.5–4.0, $FeSO_4$ dosages of 2.5–4 g/L, and $H_2O_2$ dosages of 100–150 ml/L, with stirring times of at least 90 minutes. Deviations from these conditions led to suboptimal or negative COD reductions, demonstrating the impor-tance of precise control over operational variables. These findings provide a foundation for the development of scalable and efficient oily sludge treatment methods. The experiments reveal that achieving optimal COD reduction requires careful calibration of pH, oxidant dosage, and stirring time. Having low pH, adequate $H_2O_2$ dosage, and extended stirring time ensures the most effective combination. Conversely, standalone reagents like $FeSO_4$ or excessive oxidant dosages without optimal pH fail to deliver significant impro-vements.

## Conclusions

This study investigated the influence of key parameters, including pH, hydrogen peroxide ($H_2O_2$) dosage, stirring time, and ferrous sulfate ($FeSO_4$) as a catalyst, on chemical oxygen demand (COD) reduction in oily sludge samples. The results revealed

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that a low pH of 1.5 and an $H_2O_2$ dosage of 100 ml/L were optimal for achieving a maximum COD reduction of 57%. Acidic conditions significantly enhanced oxidative degradation, but increasing $H_2O_2$ dosage beyond the optimal threshold led to diminishing returns. Experiments with $FeSO_4$ alone demonstrated limited efficacy, with higher doses unexpectedly increasing COD levels, indicating that $FeSO_4$ is ineffective as a standalone reagent and is better suited as a catalyst alongside $H_2O_2$. Stirring time was also found to be critical; without reagents, low pH conditions and stirring reduced COD minimally, with results plateauing beyond 69 minutes. However, incorporating $H_2O_2$ significantly improved COD reduction with extended stirring, achieving a maximum reduction of 30% at 90 minutes. These findings underscore the importance of optimizing reaction time for complete oxidative degradation. The optimal conditions identified that a pH of 1.5, $H_2O_2$ dosage of 100 ml/L, and 90 minutes of stirring achieved the highest COD reduction. This highlights the need for a balanced approach in advanced oxidation processes (AOPs) to enhance wastewater treatment efficiency. This research provides actionable insights for optimizing AOPs and wastewater treatment practices. Future work should explore the synergistic effects of $FeSO_4$ and $H_2O_2$, the scalability of these conditions in real-world settings, and the environmental impact of residual by-products. These efforts can contribute to developing sustainable and effective wastewater treatment technologies.

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## References

ABBASI M., DEHGHANI M., MOUSSAVI G., & AZHDARPOOR A. (2015) Degradation of organic matter of municipal sewage sludge using ultrasound treatment in shiraz wastewater treatment plant. Health Scope, 4(1). https://doi.org/10.17795/jhealthscope-23507

ABBASSI B., LIVINGSTONE T. (2019). A comparative review and multi-criteria analysis of petroleum refinery wastewater treatment technologies. Environmental Research Engineering and Management, 74(4). https://doi.org/10.5755/j01.erem.74.4.21428

AJAO A., YAKUBU S., UMOH V., & AMEH J. (2013). Bioremediation of refinery wastewater using immobilisedburkholderiacepacia and corynebacteriumsp and their transconjugants. Journal of Xenobiotics, 3(1), 4. https://doi.org/10.4081/xeno.2013.e4

AKINTAYO C., AREMU O., IGBOAMA W., NELANA S., AYANDA O. (2021). Performance evaluation of ultraviolet light and iron oxide nanoparticles for the treatment of synthetic petroleum wastewater: kinetics of COD removal. Materials, 14(17):5012. https://doi.org/10.3390/ma14175012

APPIA F., OUATTRA N. (2023) Degradation of pharmaceuticals from simulated and real hospital wastewater applying conventional Fenton process: optimization conditions and application. . https://doi.org/10.21203/rs.3.rs-290549 7/v1

AWALUDDIN A., SONIA O., LINGGAWATI A., SIREGAR S. (2021) Preliminary study on COD removal on the treatment of palm oil mill effluent (pome) using birnessite-type manganese oxide via a solvent-free method..https://doi.org/10.2991/assehr.k.210305.023

BAUTISTA P., MOHEDANO A., CASAS J., ZAZO J., RODRÍGUEZ J. (2008) An overview of the application of fenton oxidation to industrial wastewaters treatment. Journal of Chemical Technology & Biotechnology, 83(10): 1323-1338. https://doi.org/10.1002/jctb.1988

BIEŃ B., BIEŃ J. (2022). Analysis of reject water formed in the mechanical dewatering process of digested sludge conditioned by physical and chemical methods. Energies, 15(5):1678. https://doi.org/10.3390/en15051678

COSTAMAGNA P., ROSELLINI S., LAVARONE A., SCARSI G., SATURNO E., & MANTELLI V. (2021) Experimental study of a reverse osmosis pilot plant for reuse of refinery wastewater. Journal of Chemical Technology and Biotechnology, 96(10):2852-2864. https://doi.org/10.1002/jctb.6836

CUI K., SHENG X., MENG Q., SHANG G., GUO K. (2023) Effects of bioaugmentation on the performance of industrial-scale activated sludge sequencing batch reactor under load shock of heavy oil refinery wastewater. IOP Conference Series Earth and Environmental Science, 1135(1):012023. https://doi.org/10.1088/1755-1315/1135/1/ 012023

CUI K., XU Q., SHENG X., MENG Q., SHANG G., MA Y., GUO K. (2021) The impact of bioaugmentation on the performance and microbial community dynamics of an industrial-scale activated sludge sequencing batch reactor under various loading shocks of heavy oil refinery wastewater. Water, 13(20):2822. https://doi.org/10.3390/w13202822

DOI: 10.6092/issn.2281-4485/20955

DAWCZAK P., DUDZIAK M. (2020) Treatment of wastewater from the foundry industry using fenton process. Architecture Civil Engineering Environment, 13(1):115-120. https://doi.org/10.21307/acee-2020-009

EMOYAN O., AKPORHONOR E., AKPOBORIE I. (2008) Environmental risk assessment of river ljana, ekpan, delta state Nigeria. Chemical Speciation and Bioavailability, 20(1):23-32. https://doi.org/10.1080/09542299.2008.11073770

GASIM H., KUTTY S., ISA M., ALEMU L. (2013) Optimization of anaerobic treatment of petroleum refinery wastewater using artificial neural networks. Research Journal of Applied Sciences Engineering and Technology, 6(11):2077-2082. https://doi.org/10.19026/rjaset.6.3827

HAYDER G., MEGAT A., SHAMSUL R. (2014) Treatment of petroleum refinery wastewater using extended aeration activated sludge. International Journal of Engineering Research in Africa, 13:1-7. https://doi.org/10.4028/www.scientific.net/jera.13.1

HONG-YAN M., ZHANG M., SUN S., ZHANG S., LUO Y., ZHANG Z., JIANG Q. (2021) Pilot-scale airlift bioreactor with function-enhanced microbes for the reduction of refinery excess sludge. International Journal of Environmental Research and Public Health, 18(13):6742. https://doi.org/10.3390/ijerph18136742

INDIAN STANDARD 3025- Part 58 (2006) Methods of sampling and test (physical and chemical) for water and wastewater; chemical oxygen demand (COD) (RA 2017).

JAFARINEJAD S. (2019) Simulation for the performance and economic evaluation of conventional activated sludge process replacing by sequencing batch reactor technology in a petroleum refinery wastewater treatment plant. Chemengineering, 3(2):45. https://doi.org/10.3390/chemengineering3020045

JEREZ S., MARTÍN J., VENTURA M., PARIENTE M., SEGURA Y., PUYOL D., MARTÍNEZ F. (2023) Thermal hydrolysis of solid fraction reduces waste disposal and provides a substrate for anaerobic photobiological treatment of refinery wastewater. Environmental Science Water Research and Technology, 9(4):1108-1114. https://doi.org/10.1039/d2ew00263a

KNIGHT M. (2021) Assessing the performance of a $UV/H_2O_2$ process for removing toc from petroleum refinery wastewater and the respirometric effects of adding $UV/H_2O_2$ treated wastewater to activated sludge from the refinery wwtp biological treatment process.. https://doi.org/10.32920/ryerson.14644851

KULIĆ A., BEČELIĆ-TOMIN M., KERKEZ Đ., MILIDRAG G., GVOIĆ V., PRICA M., DESIGN N. (2018) Examination of the application possibilities of waste red mud in treatment of colored effluent., 175-180. https://doi.org/10.24867/grid-2018-p21

PROROT A., ESKICIOGLU C., DROSTE R., DAGOT C., LEPRAT P. (2008) Assessment of physiological state of microorganisms in activated sludge with flow cytometry: application for monitoring sludge production minimization. Journal of Industrial Microbiology and Biotechnology, 35 (11):1261-1268. https://doi.org/10.1007/s10295-008-0423-9

RIVAS J., BELTRÁN F., GIMENO O., FRADES J. (2001) Treatment of olive oil mill wastewater by fenton's reagent. Journal of Agricultural and Food Chemistry, 49(4): 1873-1880. https://doi.org/10.1021/jf001223b

SOLAK M. (2023) Application of classical fenton process and advanced photo electro fenton process for the degradation of cod from wood processing wastewater: a comparative study. Sakarya University Journal of Science, 27(3): 512-522. https://doi.org/10.16984/saufenbilder.1173306

TONY M., BEDRI Z. (2014) Experimental design of photo-fenton reactions for the treatment of car wash wastewater effluents by response surface methodological analysis. Advances in Environmental Chemistry, 1-8. https://doi.org/10.1155/2014/958134

TRAPIDO M., KULIK N., GOI A., VERESSININA Y., MUNTER R. (2009) Fenton treatment efficacy for the purification of different kinds of wastewater. Water Science and Technology, 60(7): 1795-1801. https://doi.org/10.2166/wst.2009.585

VIGGI C., PRESTA E., BELLAGAMBA M., KAČIULIS S., BALIJEPALLI S., ZANAROLI G., AULENTA F. (2015). The "oil-spill snorkel": an innovative bioelectrochemical approach to accelerate hydrocarbons biodegradation in marine sediments. Frontiers in Microbiology, 6. https://doi.org/10.3389/fmicb.2015.00881

WANG J., ZHAO Q., JIN W., JING L. (2008) Mechanism on minimization of excess sludge in oxic-settling-anaerobic (osa) process. Frontiers of Environmental Science and Engineering in China, 2(1):36-43. https://doi.org/10.1007/s11783-008-0001-4

YIN Y., WANG J. (2016) Fermentative hydrogen production from waste sludge solubilized by low-pressure wet oxidation treatment. Energy and Fuels, 30(7):5878-5884. https://doi.org/10.1021/acs.energyfuels.6b01034