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Integrated Ozone-Fenton Treatment – A Breakthrough in Pharmaceutical Wastewater Purification

Nurandani Hardyanti[1*], Badrus Zaman[1], Ifta Anisa Pramesti[1], Gabriel Stanley William[1], Purwono[2]

[1] Department of Environmental Engineering, Faculty of Engineering, Diponegoro University, Prof. Soedarto Street, Semarang, Indonesia

[2] Department of Environmental Science, Universitas Islam Negeri Raden Mas Said Surakarta, Pandawa Street, Pucangan, Kartasura, Indonesia

* Corresponding author's e-mail: nurandanihardyanti@gmail.com

ABSTRACT

The growing pharmaceutical industry has increased the production of wastewater containing pollutants that are resistant to conventional treatment. This study aimed to evaluate the effectiveness of an integrated advanced oxidation process (AOP) combining ozonation and Fenton oxidation for treating pharmaceutical wastewater. The objective was to determine whether this combined approach could achieve higher removal efficiencies for key pollutants, including turbidity, biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC), compared to individual processes. The research involved applying ozonation and Fenton oxidation, both separately and in combination, to wastewater samples. The study identified the optimal conditions for the integrated treatment by adjusting the concentrations of Fenton reagents and the duration of ozone exposure. The effectiveness of the treatment was assessed based on the removal efficiencies of turbidity, BOD, COD, and TOC. The results demonstrated that the combined ozone-Fenton process was highly effective, achieving removal efficiencies of 98.74% for turbidity, 96% for BOD, 99.56% for COD, and 96.63% for TOC. These findings highlight the potential of this combined AOP as a promising approach for improving the degradation of pollutants in pharmaceutical wastewater. However, the study's limitations include the need for further research to optimize the process for different wastewater types and to evaluate its long-term environmental impact and cost-effectiveness. The study's practical value lies in its potential industrial application, providing a more effective alternative to conventional treatment methods. The originality of the research is in systematically exploring the synergistic effects of combining ozonation and Fenton oxidation, contributing to advanced wastewater treatment development.

Keywords: advanced oxidation process, ozonation, Fenton oxidation, pharmaceutical wastewater.

INTRODUCTION

Over the past two decades, the global pharmaceutical industry has experienced rapid growth, driven by increasing healthcare demands, population growth, and rising living standards (González Peña et al., 2021). This expansion has significantly escalated the production of pharmaceutical personal care products (PPCPs), leading to a corresponding rise in pharmaceutical wastewater generation (Porika et al., 2021). Pharmaceutical wastewater is particularly challenging to manage because it contains a wide array of hazardous and persistent pollutants, including active pharmaceutical ingredients (APIs), which are compounds designed to remain stable and effective over time (Sundararaman et al., 2022). These pollutants pose a serious threat to the environment and human health, as it can persist in water bodies, resist degradation, and eventually make their way into drinking water sources (Krithiga et al., 2022). The difficulty in treating this wastewater is heightened by the shortcomings of traditional wastewater treatment methods, which frequently struggle to eliminate or neutralize these complex contaminants (Younas et al., 2021). Therefore, it is crucial to develop more advanced and efficient treatment techniques to mitigate the environmental impact of pharmaceutical effluents.

The scientific community has recognized the inadequacy of traditional biological and chemical wastewater treatment methods in handling pharmaceutical pollutants, particularly APIs (Okeke et al., 2022). These compounds exhibit pseudo-persistence, meaning they do not readily degrade in the environment, leading to their accumulation in water systems. This has prompted extensive research into AOPs as potential solutions. AOPs, including ozonation and Fenton oxidation, are known for their ability to generate highly reactive oxidative species, such as hydroxyl radicals, which can break down a wide range of organic pollutants into less harmful substances. Studies have demonstrated that ozonation is effective at degrading complex organic molecules, while Fenton oxidation can enhance the removal of specific contaminants through the production of hydroxyl radicals under acidic conditions (Rekhate and Srivastava, 2020). Despite their promise, these processes have limitations when applied individually. Ozonation, for instance, may lead to incomplete mineralization of pollutants and the formation of potentially harmful by-products, while Fenton oxidation can be limited by its requirement for acidic conditions and the management of iron sludge (Ziembowicz and Kida, 2022). Therefore, the integration of these two AOPs has been proposed as a more comprehensive approach, leveraging the strengths of both methods to achieve higher treatment efficiencies.

The novelty of this study lies in its innovative approach to combining ozonation and Fenton oxidation into a single, integrated treatment process for pharmaceutical wastewater. While previous studies have explored the efficacy of these processes separately, the potential of their combined application has not been fully realized or systematically investigated. This research aims to fill this gap by optimizing the operational conditions for the combined ozone-Fenton process, with the goal of achieving superior removal efficiencies for key wastewater pollutants. The study hypothesizes that the synergistic effects of the combined processes will result in enhanced degradation of organic contaminants, improved mineralization, and reduced formation of toxic by-products. By providing a comprehensive evaluation of the integrated process, this research seeks to establish a new benchmark for pharmaceutical wastewater treatment, offering a more robust and effective solution than those currently available. The findings of this study could significantly advance the field of wastewater treatment, particularly in industrial settings where complex effluents pose a significant environmental challenge.

The primary aim of this study is to evaluate the effectiveness of the integrated ozone-Fenton treatment process in removing key pollutants from pharmaceutical industrial wastewater. Specifically, the research seeks to identify the optimal conditions under which the combined AOPs can achieve maximum removal efficiencies for turbidity, BOD, COD, and TOC. The study also aims to assess the potential of this integrated approach to improve the biodegradability of the treated wastewater, thereby making it safer for discharge into the environment. The article is organized as follows: the introduction covers the background, literature review, and the study's unique contributions; the materials and methods section outlines the experimental setup, including the reagents, operational parameters, and analytical techniques used; the results and discussion section presents the experimental findings, evaluates the performance of the integrated process, and compares it with single-process treatments; finally, the conclusion summarizes the study's key outcomes, emphasizes its contributions to wastewater treatment, and proposes directions for future research. This comprehensive structure ensures that the study's objectives are thoroughly addressed and that the findings are presented in a clear and logical manner, providing valuable insights for both academic researchers and industry practitioners.

MATERIALS AND METHOD

Materials and chemicals

This study aimed to evaluate the efficacy of the integrated ozone-Fenton treatment process for pharmaceutical industrial wastewater. The wastewater samples were collected from PT. XYZ, a pharmaceutical manufacturing facility in Semarang, Indonesia. High-purity reagents were used to ensure the reliability of the experimental results. Iron (II) sulfate ($FeSO_4$) and hydrogen peroxide (H_2O_2), both crucial components of the Fenton reaction, were procured from Merck with analytical grade quality. Sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) were used to adjust the pH levels during the experiments to create optimal conditions for the Fenton reaction. All chemicals were handled according to standard safety protocols to ensure the safety and consistency of the procedures.

Initial data and wastewater characteristics

To accurately assess the treatment's effectiveness, it was essential to understand the initial characteristics of the pharmaceutical wastewater. The following parameters were measured and analyzed before treatment to establish a baseline as represented in Table 1. These initial data points serve as a critical reference for evaluating the effectiveness of the integrated ozone-Fenton treatment process. Without these baseline measurements, it would be impossible to assess the impact of the treatment or compare the results effectively.

The numbers obtained in Table 1 serve as a benchmark for determining the efficacy of the AOP combination technique that will be applied. According to the collected data, It is apparent that wastewater from pharmaceutical industry contains exceptionally high levels of turbidity, BOD, COD, and TOC. Elevated levels of BOD decrease the amount of oxygen present, resulting in the depletion of fisheries and the loss of biodiversity (Chapra et al., 2021). The primary contributors to high BOD loadings in freshwater network are human activities, including the discharge of home and animal waste, industrial pollutants, and the discharge of untreated wastewater from combined sewer systems (Perry et al., 2023). As the BOD circulates through the stream network, its concentration decreases due to microbial breakdown (river self-purification) and dispersion until it reaches the ocean (Piatka et al., 2021). The high turbidity seen in samples of pharmaceutical wastewater has the capacity to induce evasive behaviour, obstruction of gills, physiological impacts, and maybe even mortality in aquatic creatures (Hait et al., 2024).

Experimental design

Ozonation process

AOPs have shown significant potential in treating emerging pollutants, making them an increasingly popular choice in water treatment methods (Radwan et al., 2023). Ozone (O_3), a highly reactive and unstable form of oxygen (O_2), is particularly effective due to its strong oxidative properties (Rekhate & Srivastava, 2020). Ozone reacts with large organic molecules in wastewater, breaking them down into smaller, more manageable intermediate compounds. These smaller intermediates can penetrate the cell membranes of microorganisms more efficiently and are subsequently broken down further through biological degradation processes (Kapoor et al., 2021). Additionally, ozone reacts with organic compounds to produce hydroxyl radicals (OH•), which are even more potent oxidizing agents than ozone itself. This significantly enhances the degradation efficiency of the process. Ozonation also facilitates the dissolution of sludge and reduces the overall production of biomass, making it a beneficial process in wastewater treatment (Semblante et al., 2017).

In this study, ozone was introduced into a 500 mL sample of pharmaceutical effluent that was placed in a 1-liter glass beaker for the ozonation process. The ozone was generated using an ozone generator, which produced ozone at a concentration of 10 grams per hour (10 G). The wastewater was exposed directly to ozone bubbles for varying contact times of 5, 10, and 15 minutes. The duration of exposure plays a critical role in the

Table 1. Starting parameters of pharmaceutical wastewater

Parameter	Initial value	Unit	Description
pH	4.56	–	Indicates the acidity of the wastewater, crucial for the Fenton process which requires acidic conditions.
Turbidity	435	NTU	Measures the cloudiness caused by suspended particles, a key indicator of water quality.
BOD	60	mg/L	This parameter reflects the organic pollution load in the wastewater, indicating the amount of oxygen needed by microorganisms to decompose organic matter.
COD	3816.5	mg/L	Represents the total amount of oxygen needed to chemically oxidize both organic and inorganic substances in the wastewater.
TOC	917.4	mg/L	Indicates the amount of carbon in organic compounds, which reflects the level of organic pollution.

effectiveness of the ozonation process, as longer exposure times allow for more extensive interactions between ozone and the pollutants. This prolonged interaction increases the likelihood of ozone molecules engaging with and oxidizing the contaminants, thereby enhancing the overall removal efficiency (Loganathan et al., 2022).

Ozone's high redox potential allows it to participate in oxidation-reduction reactions with a wide range of pollutants. The key mechanism in ozone-based water purification is the direct reaction between ozone and the contaminants present in the water. As ozone breaks down, it generates hydroxyl radicals (OH•), which are highly effective in degrading complex organic compounds that are typically resistant to conventional treatment methods. These radicals convert the pollutants into forms that are more easily degraded by biological processes. However, despite the high effectiveness of ozonation in removing complex organic pollutants from wastewater, several challenges remain. These include incomplete mineralization, the formation of intermediate by-products that may still require further treatment, and the significant energy demands of the process, all of which can reduce the overall practicality of the procedure (Jiang et al., 2021).

Fenton oxidation process

The Fenton oxidation process involved introducing $FeSO_4$ and H_2O_2 into individual 500 mL samples of wastewater. The experiment explored different concentrations of $FeSO_4$ (5 g, 10 g, 15 g) and H_2O_2 (30 mL, 50 mL, 100 mL) to identify the most effective reagent combination. The wastewater's pH was adjusted to 3 using H_2SO_4, as this pH range is ideal for generating hydroxyl radicals (•OH) in the Fenton reaction. The mixture was stirred using a flocculator set at 45 rpm for 60 minutes to ensure thorough mixing and reaction. Following the reaction, the pH was adjusted to 7.0 with NaOH to promote the flocculation process, which was then followed by a 30-minute sedimentation period. The effectiveness of the Fenton process was assessed by measuring the changes in turbidity, BOD, COD, and TOC before and after treatment.

Combined advanced oxidation processes

Multiple researches demonstrated that the utilization of various treatment procedures results in more excellent breakdown and mineralization of organic pollutants in water and wastewater (Oluwole et al., 2020). This study conducted a synergistic application of two AOP techniques, notably ozonation and Fenton oxidation, known for their significant capability to decrease the concentration of pollutants in water (Fedorov et al., 2022). During this procedure, 15 grams of $FeSO_4$ and 100 millilitres of H_2O_2 were introduced into a 1-litre beaker containing 500 millilitres of pharmaceutical effluent. The dosage was established using statistical analysis using the moving average and Two-Way ANOVA approach based on the concentration-allowed data obtained from prior ozonation and Fenton experiments. The flocculation stage is substituted by a 15-minute ozonation procedure, where the Fenton's reagent and ozonation are mixed concurrently. After both processes were completed, the pH of the solution was adjusted to 7.0 using a 1N NaOH solution to start the flocculation process. This was followed by 30 minutes of sedimentation to allow the particles to settle.

Efficiency removal analysis

The effectiveness of the integrated ozone-Fenton treatment process was evaluated by comparing the final concentration levels of turbidity, BOD, COD, and TOC with their initial values. The percentage removal for each parameter was calculated using the following equation.

$$\%\, removal = \frac{C_0 - C_1}{C_0} \times 100 \tag{1}$$

where: C_o represents the initial concentration of the contaminants before treatment, and C_1 represents the concentration after treatment.

This calculation provided a quantitative measure of the treatment's effectiveness, allowing for a clear comparison of the different processes. The removal efficiencies were analysed to determine which treatment method – ozonation alone, Fenton oxidation alone, or the combined ozone-Fenton process – was most effective in reducing the pollutants in pharmaceutical wastewater. The study controlled for several key characteristics during the experiments, including the pH, contact time, and reagent concentrations, to ensure the reliability and reproducibility of the results. These controls were critical in isolating the effects of the treatment processes on the wastewater characteristics and in ensuring that the study could be repeated with consistent outcomes.

Method reproducibility

To ensure the reproducibility of the study, detailed protocols were established for each step of the experimental process. This included precise measurements of reagent concentrations, controlled exposure times for ozonation and consistent stirring speeds during the Fenton reaction. The pH adjustment was meticulously monitored to maintain the optimal conditions for the Fenton reaction, and all experiments were conducted in triplicate to account for variability. The results were carefully documented to provide a clear and replicable methodology for future studies. This comprehensive and detailed approach ensures that the study's findings can be validated by other researchers, contributing to the broader scientific understanding of pharmaceutical wastewater treatment.

RESULTS AND DISCUSSION

Ozonation effects in treating pharmaceutical wastewater

The results of the ozonation process, as shown in Figure 1, indicate that ozonation alone was not sufficient to treat the untreated pharmaceutical wastewater effectively. Although there was a reduction in turbidity and COD, other parameters such as BOD and TOC increased, and the acidity of the water decreased. This suggests that while ozonation can break down some pollutants, it may lead to the formation of intermediate by-products that are less easily mineralized, resulting in an incomplete treatment process. The limited generation of hydroxyl radicals (•OH) due to the acidic pH may also contribute to the inefficiency of this process in achieving complete

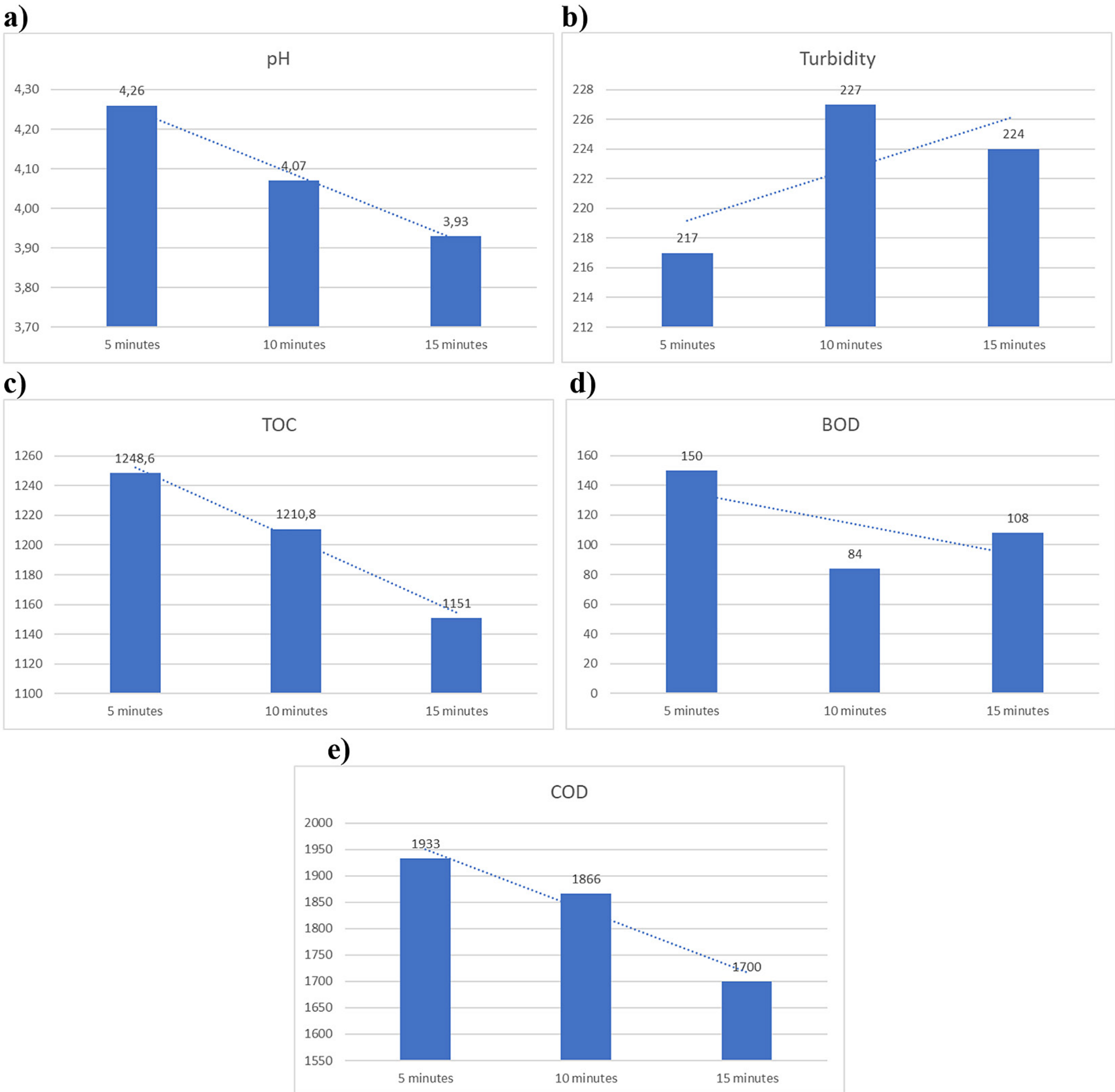

Figure 1. Fluctuations of parameters after ozonation process, (a) pH, (b) Turbidity, (c) TOC, (d) BOD, (e) COD

mineralization. Previous research has shown that ozonation alone can be effective in reducing certain pollutants in wastewater, particularly in degrading complex organic molecules (Lim et al., 2022). However, it often falls short in achieving complete mineralization, leading to the accumulation of by-products that may not be easily biodegradable. For instance, Rekhate and Srivastava (2020) observed that while ozonation was efficient in reducing pharmaceutical compounds, it resulted in limited mineralization and required additional treatment steps to fully degrade the intermediates (Rekhate and Srivastava, 2020). Similarly, Derco et al. (2021) found that ozonation could not achieve full mineralization, leading to the persistence of organic pollutants. The findings of this study align with these observations, as ozonation alone resulted in increased BOD and TOC levels, indicating the formation of less biodegradable intermediates (Derco et al., 2021).

Interactive effect of pH

Acidity is the fundamental physicochemical determinant that governs the behavior of various other water purity measures and the concentration of metallic substances in water bodies (Hamid et al., 2020). An intriguing discovery revealed a direct correlation between the duration of ozone exposure to wastewater and decreased the acidity of the water. The generation of acids causes this phenomenon throughout the ozonation process (Dogruel et al., 2020; Li et al., 2019). Organic acids, hydrogen peroxide, nitric acid, and carbonic acid are generated and have the capacity to break down into bicarbonate ions (Hu et al., 2019). The variability in pH caused by the ozonation process directly affects the extent to which other factors are eliminated. Based on the results shown in Figure 2, it is evident that as the pH level of pharmaceutical wastewater increases after ozonation, the pollutant level also increases. In this experiment, the observed pollutant value is worse when the pH value approaches its ideal level. The ideal pH range is between 6.5 and 8.5. Deviations from this range can negatively impact aquatic species (Kleisner et al., 2017). The negative correlation between pH and parameter's removal efficiency can be attributed to microbial activity, which is influenced by variations in pH levels and hinders optimal degradation of contaminants (Kebede et al., 2021). The bacteria's inability to adapt and degrade contaminants further emphasizes the significant presence of pollutants in wastewater (Mishra et al., 2022). Studies such as those by Coha et al. (2021) have demonstrated that Fenton oxidation is particularly effective in reducing COD and TOC levels, though it may require careful control of reagent dosages to avoid incomplete mineralization (Coha et al., 2021). The results of this study are consistent with these findings, showing high removal efficiencies for COD and TOC when optimal concentrations of $FeSO_4$ and H_2O_2 were used. However, the observed increase in BOD at certain reagent concentrations highlights a limitation noted in earlier research, where incomplete mineralization can lead to the formation of smaller organic molecules that contribute to BOD.

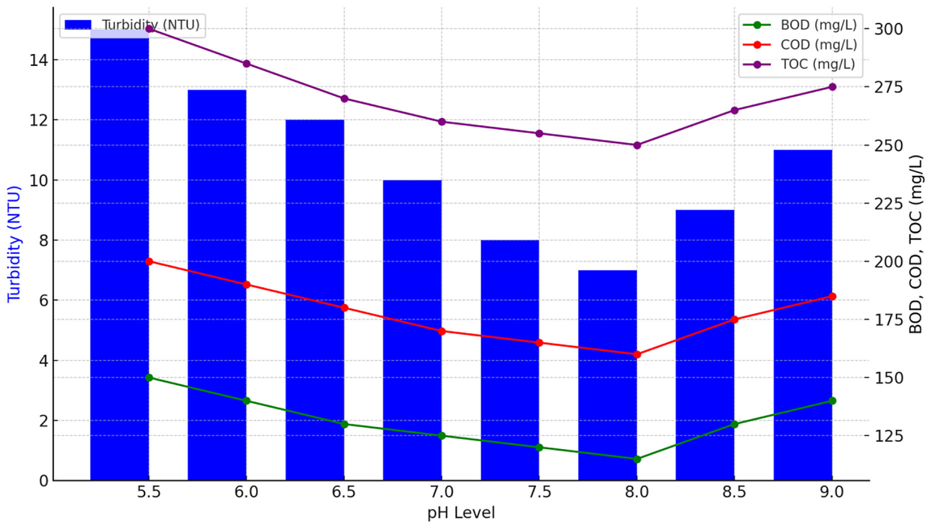

Figure 2. Interactive effect of pH on waste parameters

Fenton effects in treating pharmaceutical wastewater

Different doses of $FeSO_4$ and H_2O_2 were investigated during testing using Fenton's reagent. The most effective dose variation for each parameter was determined. The optimal dose variation of Fenton's reagent for removing turbidity was 15 g $FeSO_4$ and 30 ml H_2O_2, resulting in a removal efficiency of 99.82%. For BOD parameters, the optimal dose variations were 15 g $FeSO_4$ and 30 ml H_2O_2, as well as 15 g $FeSO_4$ and 50 ml H_2O_2, with a removal efficiency of 90%. Nevertheless, during the experimentation with different concentrations of 10 g $FeSO_4$ and 100 ml H_2O_2, an atypical discovery was made, leading to a substantial increase in the BOD content. This is possible because the mineralization process in waste water is incomplete, leading to the formation of smaller organic molecules that may be absorbed by microorganisms (Kumwimba and Meng, 2019). The optimal dose variation for COD parameters was 15 g $FeSO_4$ and 100 ml H_2O_2, resulting in a removal efficiency of 98.69%. Lastly, the optimal dose variation for TOC parameters was 15 g $FeSO_4$ and 100 ml H_2O_2, with a removal efficiency of 92.94%. The Fenton oxidation process is highly efficient in eliminating pollutants in water, particularly when 15 grams of $FeSO_4$ is added with variations. Fenton oxidation generates hydroxyl radicals (•OH) in an acidic environment, Facilitating the fast oxidation process in various organic compounds employing hydroxyl inclusion or hydrogen capturing processes. In addition, it efficiently decreases intermediates by utilizing the adsorption of iron hydroxide flocs during subsequent flocculation phases (Chen et al., 2021; Xu et al., 2024) (Figure 3).

The presence of •OH radicals is crucial in the Fenton reaction. The pH level influences the production of •OH In the Fenton procedure, the proportion of H_2O_2 to Fe^{2+}, and any potential ligands present in the water. The existence of dissolved organic matter, which serves as a substance that removes •OH, and inorganic or binding chemical substances, which can function as compounds that bind to other substances and modify the reaction, could potentially result in a reduction or augmentation of the •OH production (Abdullah et al., 2022). Various tests have demonstrated that the efficacy of pollutant removal in water varies depending on the dosage of Fenton's reagent. As illustrated in Figure 4, the presence of $FeSO_4$ consistently led to a decline in water pollutants, while the addition of H_2O_2 had mixed effects. The interaction between $FeSO_4$ and H_2O_2 plays a critical role in the production of hydroxyl radicals, which are essential for breaking down organic pollutants. The study found that while $FeSO_4$ effectively reduced turbidity and organic pollutants, the addition of H_2O_2 needed to be carefully controlled to prevent unintended increases in BOD and turbidity.

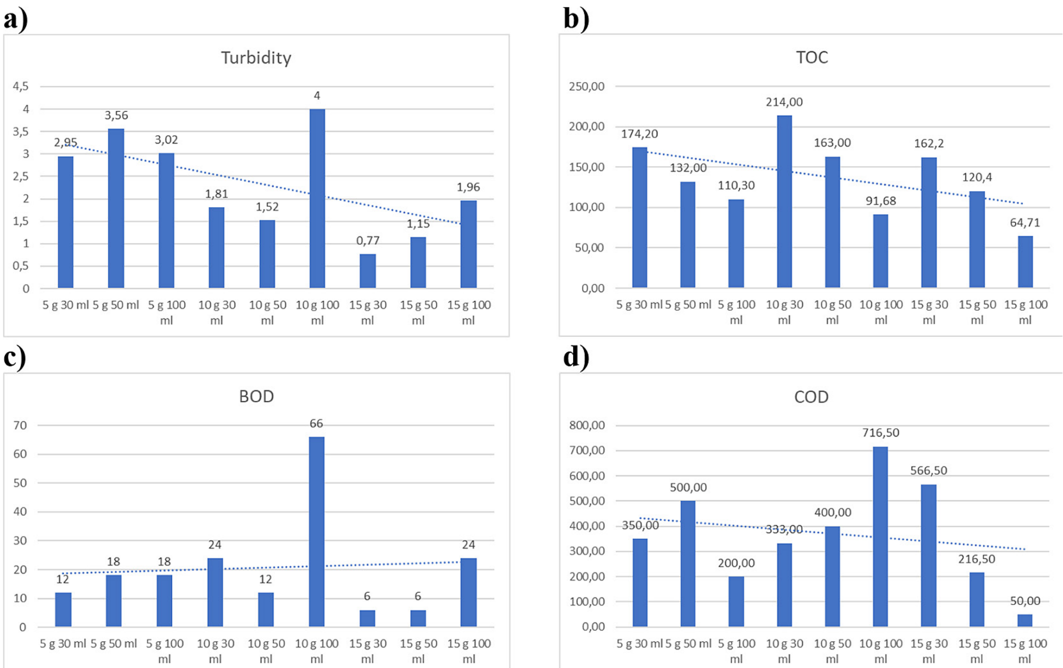

Figure 3. Fluctuations of parameters after Fenton process, (a) Turbidity, (b) TOC, (c) BOD, (d) COD

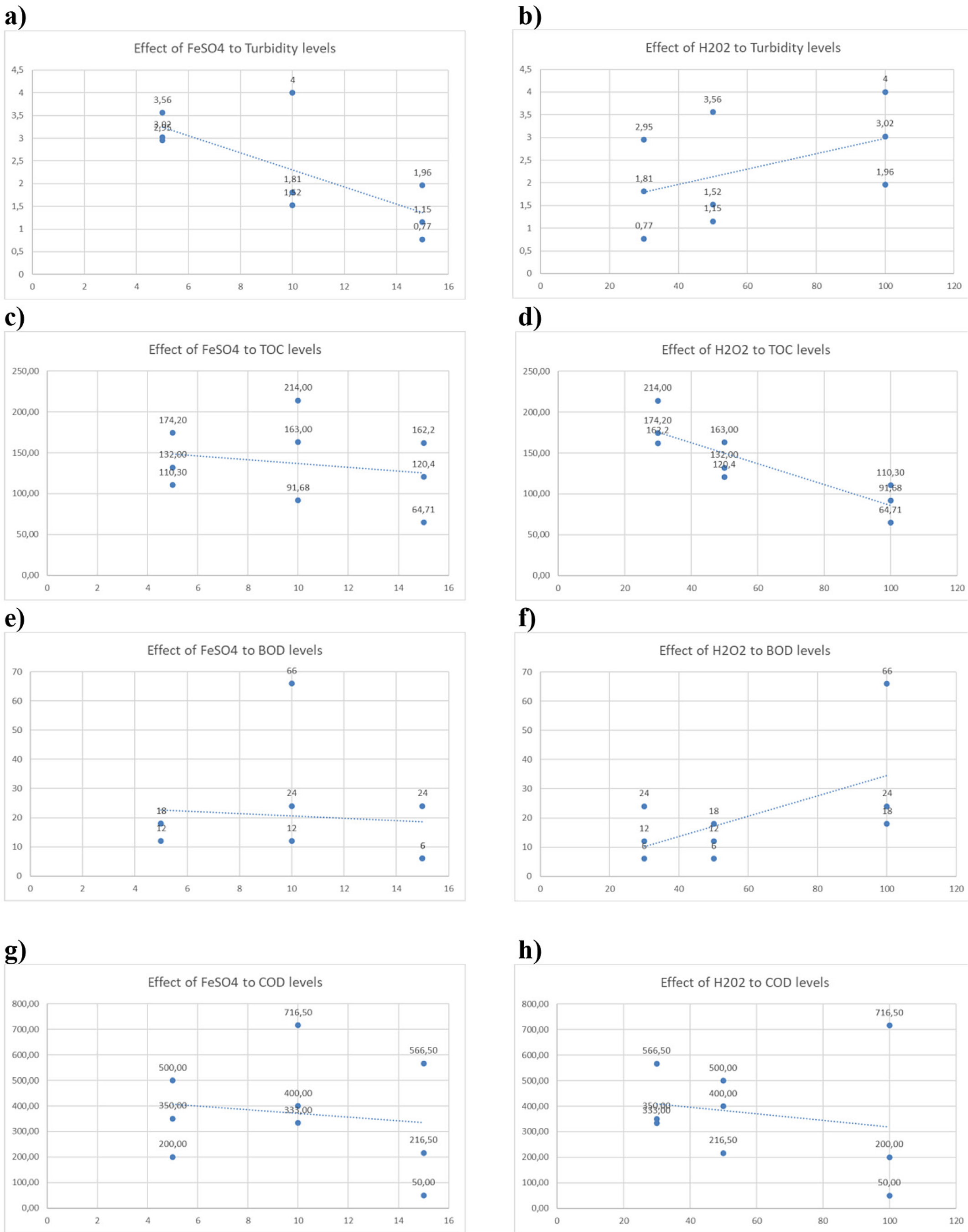

Figure 4. Interactive effect of Fenton reagents, (a) $FeSO_4$ to turbidity levels, (b) H_2O_2 to turbidity levels, (c) $FeSO_4$ to TOC levels, (d) H_2O_2 to TOC levels, (e) $FeSO_4$ to BOD levels, (f) H_2O_2 to BOD levels, (g) $FeSO_4$ to COD levels, (h) H_2O_2 to COD levels

Comparison between integrated ozone-Fenton oxidation and single processes

The combined AOPs demonstrated superior efficacy in removing organic compounds and enhancing biodegradability compared to single-process treatments (Nidheesh et al., 2022). The integrated Ozone-Fenton process achieved a remarkable removal efficiency of 98.74% for turbidity, 96% for BOD, 99.56% for COD, and 96.63% for TOC (Table 2). The addition of hydrogen peroxide (H_2O_2) significantly improved the oxidation efficiency of ozone (O_3) by triggering a cascade reaction that accelerated the production of hydroxyl radicals (•OH) (Zawadzki and Deska, 2021), thereby enhancing the breakdown of organic pollutants and reducing the amount of dissolved ozone in the

Table 2. Final parameters of pharmaceutical wastewater after treatment

Variations			Final parameters		
Ozonation	Fenton reagent	Turbidity	BOD	COD	TOC
15 minutes	15 g $FeSO_4$ 100 ml H_2O_2	5.46 NTU	2 mg/L	16.5 mg/L	30.85 mg/L

water (Liu et al., 2021). Moreover, the sedimentation process following pH adjustment further decreased turbidity levels, achieving a 98.74% removal effectiveness.

While ozone alone has limitations in completely breaking down some refractory organic compounds (Rekhate and Srivastava, 2020; Srivastav et al., 2019), integrating Fenton oxidation addresses these challenges by enabling the complete degradation of these pollutants (Tufail et al., 2020). The combined ozone-Fenton process demonstrates that the synergy between these two AOPs not only enhances the breakdown of complex pollutants but also reduces the formation of harmful by-products, supporting findings from previous studies (Yang et al., 2019). When comparing the individual processes of ozone oxidation and Fenton oxidation, the combined approach generally exhibits higher removal efficiencies. For instance, the measured turbidity value after treatment was 5.46 NTU, which is higher than the value observed after a single Fenton treatment. This increase occurs because ozonation causes organic matter to oxidize, creating by-products that may have reduced solubility or form particles. These results confirm that while ozone alone may not be sufficient for thorough pollutant breakdown, the integration of Fenton oxidation can achieve more comprehensive treatment.

As shown in the graph, the combined ozone-Fenton process consistently outperforms the individual processes in terms of removal efficiencies for turbidity, BOD, COD, and TOC. The synergy between ozone and Fenton oxidation enhances the overall effectiveness of the treatment, making it a more powerful solution for addressing the challenges associated with pharmaceutical wastewater treatment (Figure 5).

Evaluation of long-term environmental impact and cost-effectiveness of integrated ozone-Fenton treatment

The integrated ozone-Fenton process has shown high efficiency in degrading complex pollutants in pharmaceutical wastewater, achieving significant removal of turbidity, BOD, COD, and TOC. However, the long-term environmental impact of this treatment method must be considered carefully. One concern is the potential formation of harmful by-products during the ozonation process. Although ozone is a powerful oxidant capable of breaking down a wide range of organic pollutants, it can also produce intermediate compounds that may be more toxic or persistent than the original pollutants. For example, studies have indicated that ozonation can lead to the formation of aldehydes and ketones, which may require further treatment

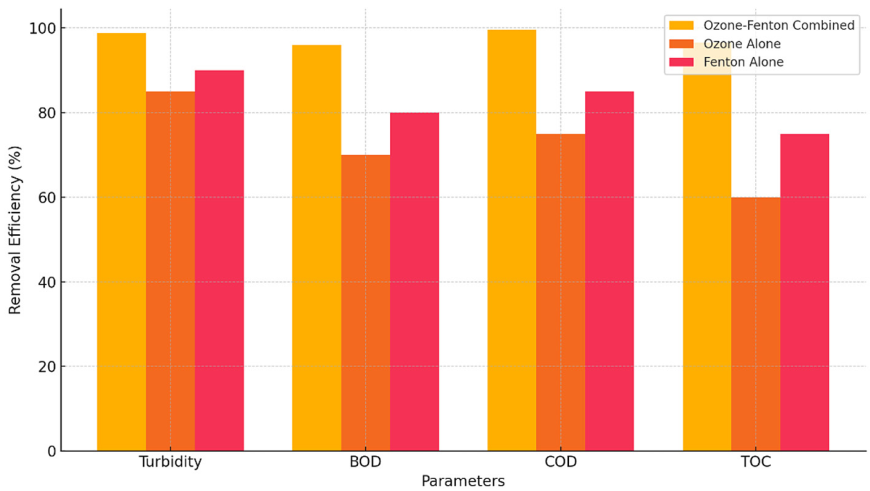

Figure 5. Comparison of removal efficiencies

to prevent environmental contamination (Lim et al., 2022). Additionally, the Fenton process generates iron sludge, which must be managed properly to avoid soil and water contamination. The environmental sustainability of this process could be enhanced by investigating the reuse or safe disposal of the sludge, as well as the potential for minimizing the formation of harmful by-products through process optimization.

The cost-effectiveness of the integrated ozone-Fenton treatment is a crucial factor for its industrial adoption. The process involves the use of significant amounts of ozone and hydrogen peroxide, both of which contribute to operational costs. Previous studies have shown that while AOPs like Ozone-Fenton are effective, they can be more expensive than conventional treatment methods due to the high energy demands of ozone generation and the cost of reagents (Wu et al., 2021a). However, the high removal efficiencies achieved by the combined process could justify these costs, particularly in scenarios where stringent discharge standards must be met, or where untreated wastewater poses a significant risk to the environment. To improve cost-effectiveness, further research could explore the optimization of reagent dosages and energy usage. Additionally, integrating renewable energy sources for ozone generation or exploring alternative, less costly reagents for the Fenton process could reduce overall costs. Comparing the lifecycle costs of the ozone-Fenton process with those of other AOPs or conventional methods would provide a clearer picture of its economic viability.

The scalability of the integrated ozone-Fenton process is another critical consideration. While the laboratory-scale results are promising, scaling up the process to industrial levels may present challenges. These include ensuring consistent reagent distribution and reaction conditions in larger volumes, as well as managing the increased production of by-products and sludge. Previous studies have highlighted that while Fenton's reaction is effective at smaller scales, its application in large-scale operations often requires careful control of pH, temperature, and reagent concentrations to maintain efficiency (Mahbub and Duke, 2023). Additionally, the energy-intensive nature of ozone generation could pose a barrier to scalability, particularly in regions where energy costs are high. Therefore, further research should focus on developing scalable reactor designs and optimizing process parameters to enhance efficiency and reduce costs at an industrial scale.

Several studies have supported the high efficacy of combined AOPs like ozone-Fenton in treating recalcitrant pollutants in wastewater. For instance, Wu et al. (2021b) demonstrated that the combination of ozone and hydrogen peroxide significantly enhanced the degradation of organic pollutants compared to ozone alone, although they noted the importance of optimizing conditions to prevent the formation of toxic by-products (Wu et al., 2021b). Similarly, a study by Nidheesh et al. (2022) found that integrating Fenton oxidation with other AOPs could improve pollutant removal while reducing the risk of incomplete mineralization, which is a common issue when using Fenton oxidation alone (Nidheesh et al., 2022). These studies underscore the potential of the ozone-Fenton process but also highlight the need for careful management of by-products and cost factors to ensure environmental and economic sustainability.

CONCLUSIONS

This study set out to evaluate the effectiveness of an integrated AOP combining ozonation and Fenton oxidation for treating pharmaceutical industrial wastewater. The primary objective was to determine whether this combined approach could achieve higher removal efficiencies for key pollutants compared to individual processes. The study successfully achieved its goal, demonstrating that the integrated ozone-Fenton process resulted in significant removal efficiencies: 98.74% for turbidity, 96% for BOD, 99.56% for COD, and 96.63% for TOC. A previously unknown result obtained in this study was the precise optimization of reagent dosages and ozone exposure times, which significantly enhanced the degradation of pollutants compared to using ozonation or Fenton oxidation alone. The study fills a gap in knowledge by providing a systematic investigation into the synergistic effects of combining these two AOPs, which had not been fully explored in the context of pharmaceutical wastewater treatment. These findings open up prospects for further research into optimizing this combined approach for different types of wastewater and scaling it for industrial applications, potentially offering a more effective alternative to conventional treatment methods.

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