

Decolorization by Catalytic Ozonation USING Mn(II) Fe(II) and Fe(III)

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Abstract: The textile industry holds significant importance in Thailand. It has been estimated that 10-20% of dyes are lost during the dyeing process and subsequently released into wastewater. The high concentration of non-biodegradable substances in these wastewaters makes them challenging to treat using conventional methods. Therefore, this study aimed to assess the effectiveness of a catalytic ozonation process employing Mn(II), Fe(II), and Fe(III) for treating synthetic dye wastewater. The study also sought to optimize operational parameters such as pH and contact time. Both with and without catalytic ozonation, experiments were conducted in a batch reactor with a consistent ozone flow rate of 6 g/hr. Under the non-catalytic ozonation conditions, it was observed that more than 90% of decolorization occurred within 15 minutes at a pH of 9. The ozonation of the dye followed a first-order reaction mechanism at room temperature, with a rate constant (k) of 0.18 min⁻¹. The catalytic ozonation used a concentration of 1.2 mM of Mn(II) was showed color removal of 90% in 8 min. For catalytic ozonation used Fe(II) and Fe(III) with concentrations of 0.6 mM showed color removal of 90% in 10 min. The highest rate constant (k) showed 0.29 min⁻¹ for Mn(II) and 0.21 min⁻¹ for Fe(II) and Fe(III). In conclusion, the study found that the inclusion of a catalyst substantially enhanced the degradation efficiency of the dye compared to ozonation without a catalyst.

Keywords: Decolorization, Dye Wastewater, Catalytic Ozonation, Advance Oxidation Process.

1. INTRODUCTION

The textile industry has played a vital role in Thailand's economic development over the past few decades. In this sector, approximately 200,000 tons of dyes are utilized. These dyes, classified as water-soluble, exhibit a loss of 10-20% during the dyeing process, ultimately released into wastewater [1]. Textile wastewater is characterized by a significant presence of refractory organic substances and color, which consist of toxic and non-biodegradable compounds [2]. Conventional technologies face challenges in effectively treating these complex wastewaters [3].

Advanced Oxidation Processes (AOPs) represent a category of chemical treatment methodologies designed for eliminating organic compounds from water and wastewater. These techniques operate by generating hydroxyl radicals, which are highly effective in purifying water. AOPs encompass various methods, including ozonation, photocatalytic degradation, the use of Fenton's reagent (comprising H₂O₂/Fe²⁺), Electro-Fenton, photo-Fenton processes, UV/chlorine treatment, and wet air oxidation. Importantly, these methods are particularly efficient in degrading organic pollutants under pressure conditions and ambient temperature.

Ozone and ozone-based advanced oxidation systems are acknowledged as potent and environmentally friendly technologies capable of efficiently degrading a broad spectrum of organic pollutants [4]. In recent years, the application of ozonation in wastewater treatment has experienced substantial growth. Significantly, ozonation stands out as the preferred technique for removing colored substances characterized by chromophore groups with conjugated double bonds. These compounds can be effectively disintegrated into smaller molecules through both

direct and indirect processes mediated by ozone.[5]. Hydroxyl radicals are produced via radical chain reactions, and these radicals react with the organic compounds, contributing to their degradation [6]. Nevertheless, there are situations in which the ozone process might not fully oxidize organic dyes to CO_2 and H_2O , resulting in the generation of partial oxidation products. In such scenarios, it is recommended to combine ozone with either homogeneous or heterogeneous catalysts to improve the removal of organic compounds. [7].

Recently, there has been a growing focus on developing catalysts to enhance the efficiency of the catalytic ozonation process. These catalysts encompass a range of materials, including transition metal ions, metal oxides, and activated carbon. For instance, [8] employed catalytic ozonation to effectively remove organic pollutants, achieving positive results when using iron shavings at initial pH values between 7.18 and 7.52. This process led to a notable reduction in COD levels, decreasing about 70 mg/L from 142 mg/L. Moreover, the toxicity of the wastewater decreased from 51% to 33%, primarily attributed to the oxidative actions of hydroxyl radicals, co-precipitation, and oxidation by other oxidants. As a result, this method has been introduced as a promising approach for the removal of organic contaminants. So, this study was to investigate the efficiency of catalytic ozonation process using Mn(II) Fe(II), and Fe(III) for treating synthetic dye wastewater and to optimize the operating condition such as contact time and pH.

2. MATERIALS AND METHODS

Materials

Methylene blue dye solutions were created by dissolving the dye in distilled water, with the initial pH set at 7. Adjustments to the pH were made using Hydrochloric acid (HCl) and sodium hydroxide (NaOH). $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4) \cdot \text{H}_2\text{O}$ were used as Mn(II), Fe(II), and Fe(III) served as catalysts in the catalytic ozonation process.

Ozonation Experiment

Ozone was generated by an ozone generator operating at a flow rate of 6 g/h and introduced into the reactor through a porous diffuser located at the bottom, generating fine bubbles. This ozonation process was conducted within a 1 L reactor. A continuous stream of ozone-oxygen gas was supplied to the reactor through a porous gas distributor. To capture any residual ozone in the off-gas, a KI solution was employed effectively. Following treatment, an assessment of color was conducted using the ADMI (American Dye Manufacturers Institute) unit. Catalytic ozonation for variation concentration of Mn(II), Fe(II) and Fe(III) was range 0.2-1.2 mM.

3. RESULTS AND DISCUSSION

The Impact of Ozonation on Decolorization

The effect of ozonation on decolorization of reaction time is illustrated in Fig. 1. The data indicates a rapid decrease in color, with approximately 80% decolorization achieved within 10 minutes. Notably, more than 50% of color reduction occurred within the first 5 minutes. However, beyond a treatment time of 20 minutes, the reduction in color became less significant, stabilizing at a 95% reduction after 60 minutes of treatment. As demonstrated, ozonation emerges as a promising and effective process for degradation.

The Influence of pH on Decolorization During Ozonation

pH is a critical factor that significantly influences the efficiency of ozonation-based treatment. The relationship between treatment time and the attainment of the desired removal percentage is depicted in Fig. 2. The effectiveness of color removal exhibits an upward trend with increasing pH levels. Specifically, 80% color removal was accomplished after 10 minutes at all pH values. However, at pH 11, the maximum color removal of 90% was achieved within the same 10-minute timeframe. The observed positive correlation between color removal and pH is ascribed to the presence of reactive radicals. At higher pH values, hydroxyl radicals are generated through ozone decomposition, while at lower pH levels, molecular ozone remains the primary oxidant. This distinction is pivotal, as hydroxyl radicals exhibit a higher oxidizing potential compared to molecular ozone, resulting in more efficient decolorization at elevated pH levels. The degradation mechanism of organic dyes is explored in the presence of hydroxyl radicals under basic pH conditions. These radicals are generated through radical chain reactions, subsequently reacting with organic compounds.[9].

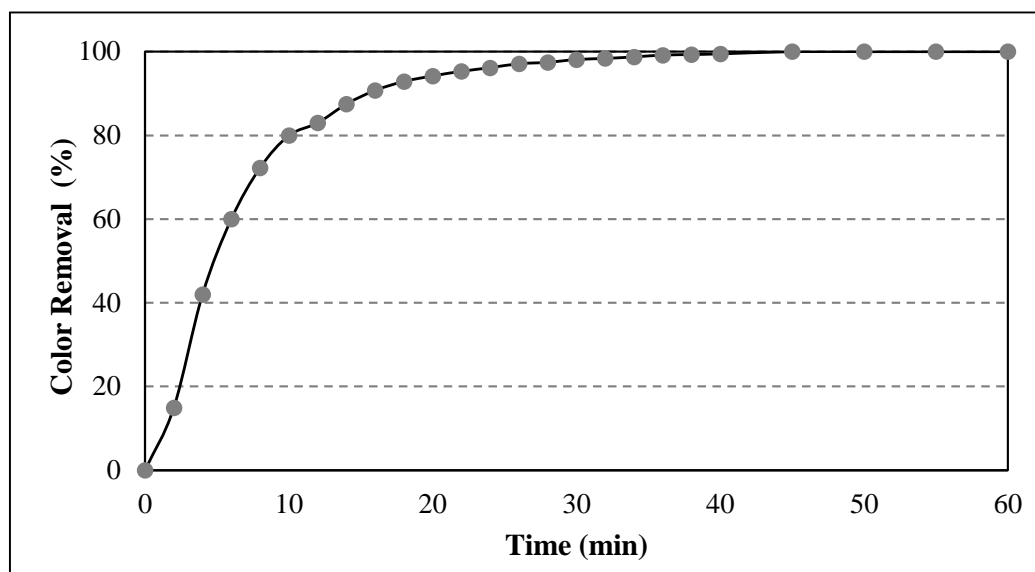


Fig. 1 Illustrates the time-dependent color removal of the dye at pH 7 and room temperature.

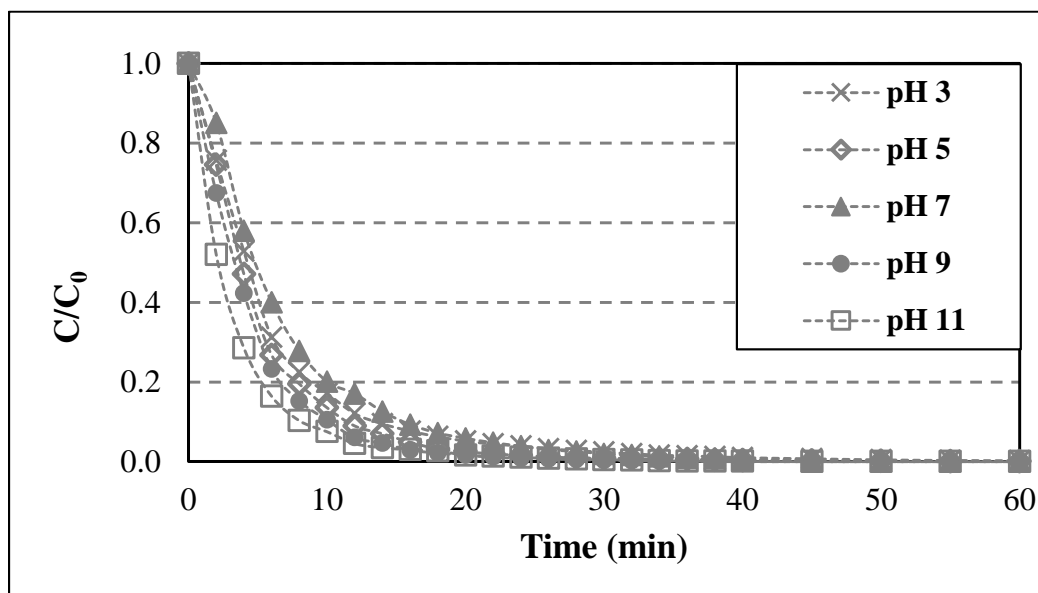
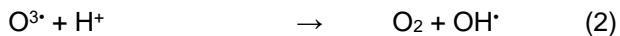


Fig. 2 The effect of pH on decolorization During ozonation

Decolorization of Ozonation with Different Catalysts

This study aimed to assess the efficiency of the catalytic ozonation process using Mn(II), Fe(II), and Fe(III) for the treatment of synthetic dye wastewater.

The decolorization of catalytic ozonation experiment with Mn(II) showed in Fig. 3 that the variation concentration of Mn(II) was 0.2-1.2 mM can significantly accelerate the decolorization rate. The removal efficiency increases from 80% to 95% after 10 min at concentration of 1.2 mM of Mn(II). The reaction of Mn(II) combine with the ozone can be generated hydroxyl radical (OH[•]), which destroy complex compounds of dye showed in equation (1-4)



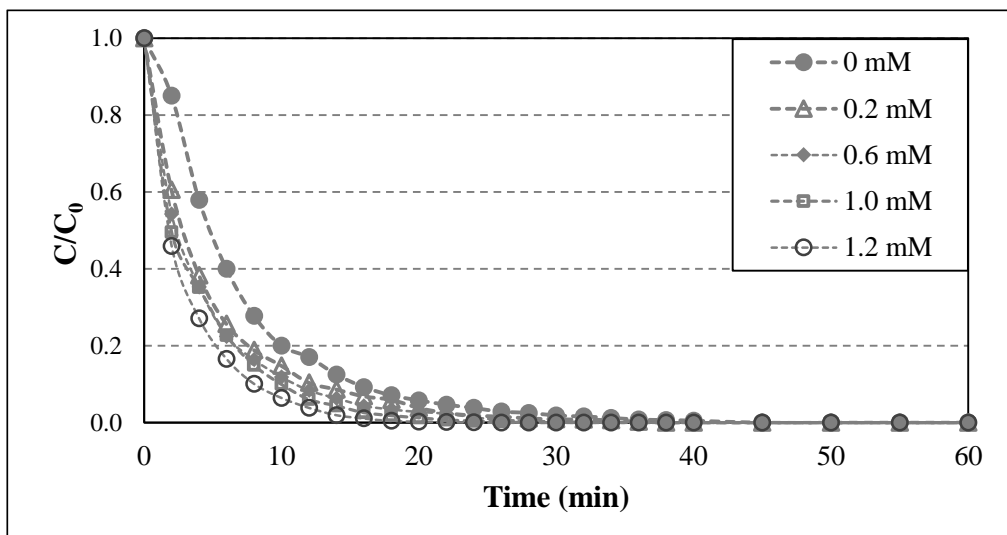


Fig. 3 The decolorization of catalytic ozonation for variation concentration of Mn(II)

For the decolorization of catalytic ozonation for variation concentration of Fe(II) was range 0.2-1.2 mM. The removal efficiency increases from 80% to 90% after 10 min at concentration of 0.6 mM of Fe(II) showed in Fig. 4. And the decolorization of catalytic ozonation for variation concentration of Fe(III) was range 0.2-1.2 mM. The removal efficiency increases from 80% to 92% after 10 min at concentration of 0.6 mM of Fe(III) showed in Fig. 5. The reaction of Fe(II) and Fe(III) combine with the ozone can be generated hydroxyl radical (OH[•]), which destroy complex compounds of dye showed in equation (5-12)

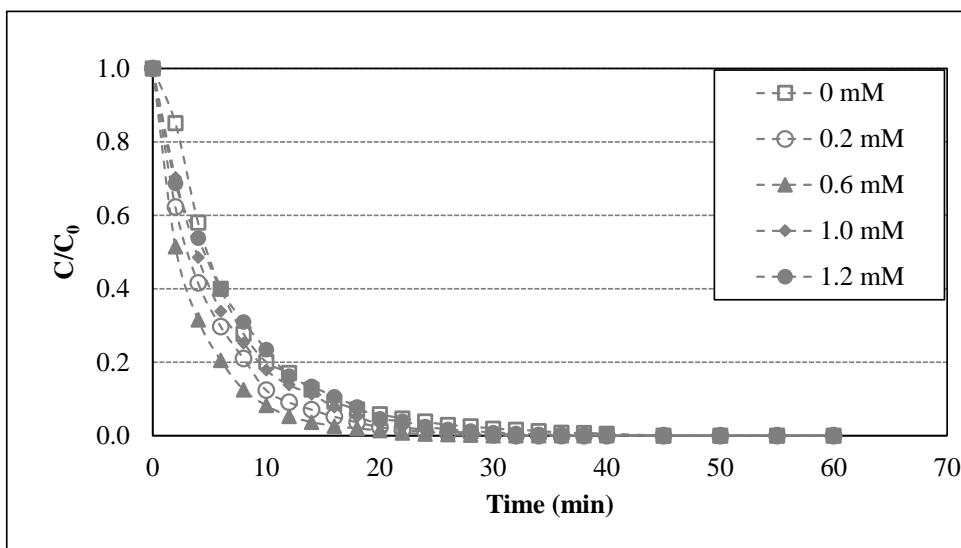
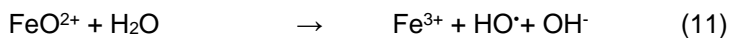
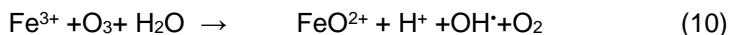
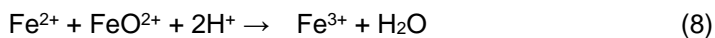
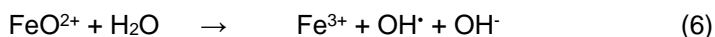


Fig. 4 The decolorization in catalytic ozonation at various concentrations of Fe(II)

The generation of hydroxyl radicals (OH^\bullet) through hydroxide ions (OH^-) and other radical initiators plays a crucial role in oxidizing organic compounds that exhibit resistance to direct molecular ozone attack. Based on these facts, in this study an increase in ozone absorption rate was attributable to the shift of the reaction mechanism from selective electrophilic attack to the OH^\bullet radical type oxidation. This suggests that the catalysts in this experiment primarily expedited the cleavage of color-generating bonds, resulting in color reduction. However, it's worth noting that these catalysts were not capable of reducing the activation energy to the extent required for breaking down the fundamental structure of the dye's backbone.

Ozonation Reaction Kinetics

It is widely acknowledged that the hydroxyl radical (OH^\bullet) resulting from ozone decomposition plays a pivotal role as the primary oxidant in the ozonation process. This is particularly significant because the amount of ozone delivered exceeded the concentration of dye. Consequently, the reaction rate equation was described by the following equation (13)

$$-r_a = -(dC_a/dt) = kC_a \quad (13)$$

The rate of dye decay is represented by dC_a/dt , where C_a is the dye concentration and k is the rate constant. Consequently, Equation (13) can be rearranged into the pseudo-first-order equation (Equation 14), where k_{pseudo} signifies the pseudo-first-order rate constant.

$$\ln(C_a/C_{a0}) = -kt \quad (14)$$

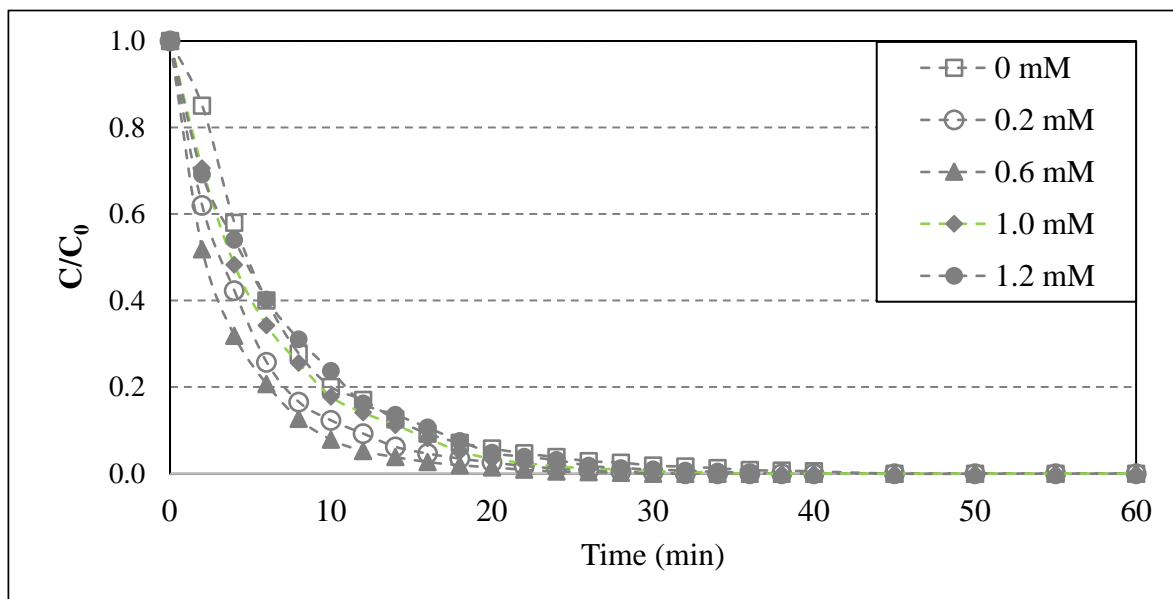


Fig. 5 The decolorization of catalytic ozonation for variation concentration of Fe(III)

The ozonation of the dye was determined to follow a first-order reaction at room temperature, with a higher color removal observed, indicated by a rate constant (k) of 0.18 min^{-1} . The catalytic ozonation used a concentration of 1.2 mM of Mn(II) was showed color removal of 90% in 8 min . For catalytic ozonation used Fe(II) and Fe(III) with concentrations of 0.6 mM showed color removal of 90% in 10 min . The highest rate constant (k) showed 0.29 min^{-1} for Mn(II) and 0.21 min^{-1} for Fe(II) and Fe(III) .

Commercial reactive azo dyes with varied structures underwent ozone treatment in a semi-batch reactor. According to Reference [10], optimal decolorization conditions were attained at $\text{pH } 10$, leading to COD removal between 95% and 99% for different dyes, indicative of the complexities in their chemical structures. The reaction kinetics followed a pseudo-first-order model. Reference [11] showed catalytic ozonation, employing $\text{Cu(NO}_3)_2$ as a catalyst demonstrated the highest efficiency, achieving 90% color removal within 48 minutes and a concurrent 60% reduction in COD . and the rate constants were 0.125 and 0.201 min^{-1} for O_3 and $\text{O}_3/\text{Cu(NO}_3)_2$ respectively.

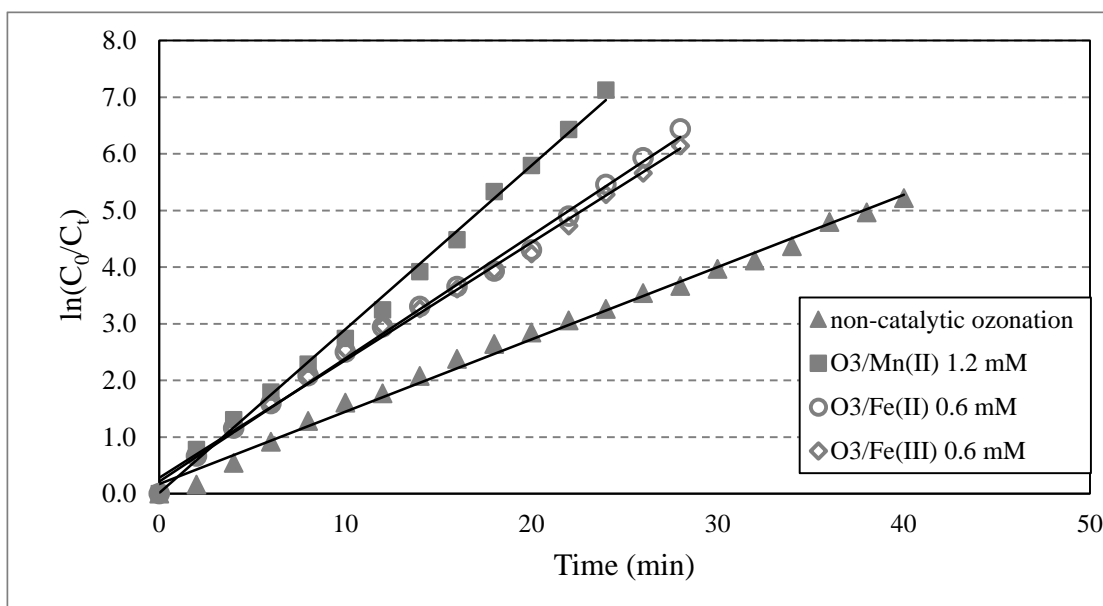


Fig. 6 The kinetics of non-catalytic and catalytic ozonation

Table 1 Rate constant of reaction by non-catalytic and catalytic ozonation

Condition	k (min ⁻¹)
Non-Catalytic Ozonation	0.18
O ₃ /Mn(II) 1.2 mM	0.29
O ₃ /Fe(II) 0.6 mM	0.21
O ₃ /Fe(III) 0.6 mM	0.21

4. CONCLUSIONS

The current study demonstrated that under non-catalytic ozonation conditions, more than 90% decolorization was achieved within 15 minutes at pH 9. The ozonation of the dye predominantly followed a first-order reaction at room temperature. Specifically, at pH 9, a higher color removal was observed, characterized by a rate constant (k) of 0.18 min⁻¹. In catalytic ozonation, using a concentration of 1.2 mM of Mn(II), a 90% color removal was achieved in 8 minutes. For catalytic ozonation with Fe(II) and Fe(III) at concentrations of 0.6 mM, a 90% color removal was accomplished within 10 minutes. The highest rate constants (k) were recorded as 0.29 min⁻¹ for Mn(II) and 0.21 min⁻¹ for Fe(II) and Fe(III). The study concluded that the presence of catalysts significantly enhanced the degradation efficiency of the dye compared to non-catalytic ozonation.

Acknowledgments

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