

DECOLORIZATION OF LIGNIN IN WASTEWATER BY CATALYTIC OZONATION USING ZINC OXIDE-COATED RIVER GRAVEL

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Received: September 20, 2025; Revised: December 01, 2025; Accepted: December 09, 2025

Abstract

This study investigated the efficiency of catalytic ozonation for decolorizing lignin in synthetic wastewater using a heterogeneous catalyst - zinc oxide (ZnO) coated on river gravel - in a continuous flow reactor. The effects of three independent variables were examined: initial lignin concentration, solution pH, and ZnO catalyst dosage. Ozonation without a catalyst achieved a maximum lignin removal efficiency of 43.38% at an initial concentration of 100 mg L⁻¹, pH 3, and a hydraulic retention time of 60 min. The reaction followed first - order kinetics with rate constants of 0.0117 min⁻¹ at pH 3 and 0.899 min⁻¹ at pH 11. Increasing the pH to 11 enhanced lignin removal to 51.75%. When ZnO/gravel catalyst was introduced at 3 g L⁻¹ and pH of 11, the lignin removal efficiency significantly improved to 94.90%, with a reaction rate constant of 2.168 min⁻¹. Across the tested pH range (3 - 11), catalytic ozonation using ZnO/gravel demonstrated consistently high decolorization efficiency, ranging from 68.25% to 94.90%.

Keywords: Lignin; Zinc oxide; Catalytic ozonation; Continuous flow

Introduction

The discharge of highly colored effluent from pulp and paper mills is widely recognized as an important environmental issue, primarily due to its influence on public perception and acceptance of wastewater quality. The coloration originates mainly from three production stages - pulp cooking, bleaching, and colored-paper manufacturing - where lignin and its derivatives are released in large quantities. Although biological treatment, particularly the activated sludge process, is commonly implemented and effective in reducing

organic and toxic loads to levels compliant with Thailand's Ministry of Industry regulations, the effluent often remains visually dark even when meeting the permitted threshold of ≤300 ADMI, creating aesthetic concerns and negative community responses, especially in dry seasons. Conventional biological treatment removes only about 30% of color, and while chemical approaches such as alum coagulation can further improve clarity, they are often limited by high operational cost, excess chemical consumption leading to

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DOI: <https://doi.org/10.55766/sujst11561>

Suranaree J. Sci. Technol. 33(3):030389(1-9)

foaming and conductivity increases, chemical residues, and difficulties in sludge dewatering. Consequently, alternative methods - such as activated carbon adsorption, ion exchange, ozonation, and chlorine - based oxidation - have been developed, with carbon adsorption, ozonation, and chlorination mostly tested at pilot scale, and ion exchange occasionally adopted in full-scale operations. Since lignin is the dominant chromophore in mill effluent and is formed by polymerization of p-coumaryl, coniferyl, and sinapyl alcohols into H, G, and S phenylpropanoid units (Fisher & Fong, 2014; Fu *et al.*, 2024), many recent studies have focused on oxidation-based destruction of lignin structures. Ozonation, a key advanced oxidation process (AOP), offers strong oxidative ability but suffers from incomplete mineralization, high energy demand, and low ozone stability in water. To improve reaction efficiency, heterogeneous catalytic ozonation has been introduced to enhance hydroxyl radical formation, thereby increasing the degradation of persistent compounds (Boczkaj and Fernandes, 2017; Ghuge and Saroha, 2018). Nanomaterials have emerged as promising catalysts due to their high surface area and reactivity, with zinc oxide (ZnO) being widely studied for its strong catalytic activity, stability, low toxicity, insolubility, and economic feasibility. Nano-ZnO exhibits efficient electron transfer and high photosensitivity (Zhu & Wang, 2025), and experimental evidence shows that it accelerates lignin breakdown through radical-driven mechanisms involving early cleavage of conjugated C=C structures (Dong *et al.*, 2022; Wei *et al.*, 2025).

In recent years, catalytic ozonation using metal oxides supported by porous media such as alumina, silica, zeolite, and glass beads has been investigated for treating various pollutants. Catalysts such as ZnO, MgCO₃, NiO, Fe₂O₃, CuO, and MnO have demonstrated effectiveness in enhancing ozonation reactions (Bashiri & Rafiee, 2014; Fu *et al.*, 2024; Yang *et al.*, 2024). Notably, ZnO has proven highly effective in the degradation of compounds such as 2,4-dichlorophenoxyacetic acid and oxalic acid. However, limited studies have explored the immobilization of ZnO on low-cost substrates like river gravel for the degradation of lignin.

This research focuses on evaluating the efficiency of catalytic ozonation using ZnO immobilized on river gravel (ZnO/gravel) as a fixed-bed heterogeneous catalyst for lignin decolorization in synthetic wastewater. The effects of key operating parameters - initial pH, catalyst dosage, and lignin concentration - were systematically investigated. In addition, the reaction

kinetics of the catalytic ozonation process were analyzed and compared to those of ozonation alone. Finally, the reusability of the ZnO/gravel catalyst and potential zinc leaching were examined to assess the sustainability and practical application of the proposed system. The key contribution of this study lies in the potential application of ZnO/gravel catalytic ozonation for broader treatment of recalcitrant organics and as a pretreatment step to enhance subsequent biological processes.

Materials and Methods

Materials and reagents

Alkaline lignin powder (99.99% purity, CAS No. 8068-05-1) was obtained from Tokyo Chemical Industry Co., Ltd. (Japan). Nitric acid (HNO₃), sodium thiosulfate (Na₂S₂O₃), soluble starch, and potassium iodide (KI) of analytical grade were purchased from KemAUS (Australia). Ozone was generated using an ozone generator (Biozone, Thailand). Potassium iodide was employed to capture residual ozone, while sodium thiosulfate and soluble starch were used for quantitative determination of ozone concentration. All stock solutions were prepared with deionized water.

Catalyst preparation and characterization

Zinc oxide (ZnO) nanopowder (25-50 nm) supplied by the College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang, Thailand, was used as the catalyst. ZnO was immobilized onto river gravel (1-3.5 mm diameter) by a sol - gel coating technique. Briefly, ZnO powder was suspended in a water-methanol mixture (1 g catalyst per 20 mL solution), and the pH was adjusted to 3.0 ± 0.1 with 1 N nitric acid. Gravel substrates were immersed in the ZnO suspension for 1 min, air-dried at room temperature for 12 h, and subsequently calcined at 500°C for 2 h. After calcination, the coated gravel was cooled, rinsed with distilled water to remove loosely bound particles, dried at 104 ± 1°C for 6 h, and stored in a desiccator prior to use.

The ZnO loading on the gravel support was determined according to Equation (1):

$$X_{Zn} = X_{S+Zn} - X_S \quad (1)$$

where X_{Zn} represents the net ZnO loading (g), X_S is the initial weight of the support (g), and X_{S+Zn} is the total weight of ZnO and support after calcination (g).

The crystallographic structure of immobilized ZnO was analyzed using X-ray diffraction (XRD). Surface morphology and elemental composition

were characterized by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX). These analyses were performed to confirm the presence, distribution, and stability of ZnO on the gravel substrates for subsequent lignin decolorization experiments.

Reactor system

The experimental setup consisted of a continuous-flow, laboratory-scale ozone bubble reactor with a cylindrical polyvinyl chloride (PVC) vessel (95 cm length $\times$ 7 cm internal diameter; effective volume 3.7 L) (Figure 1). The generator supplied an oxygen feed gas at 7.0 L min⁻¹, corresponding to an ozone production rate of approximately 83.3 mg.min⁻¹. Fine ozone bubbles were dispersed through gas diffusers located at the reactor base. Off-gas ozone was collected in trap reactors, each containing 2.50 L of acidified 2.0% potassium iodide solution for quantification of unreacted ozone.

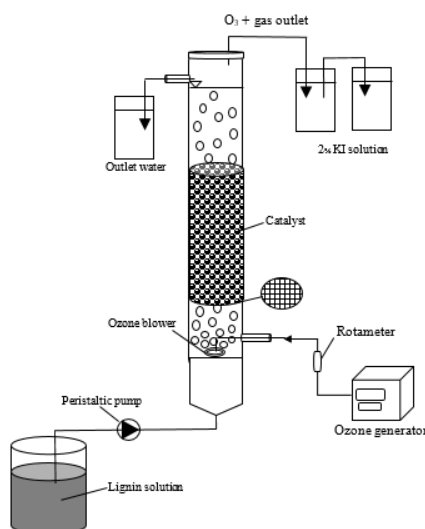


Figure 1. Schematic diagram of the experimental catalytic ozonation reactor system

Ozone was generated using an ozone generator (Biozone, Thailand) at a production capacity of 5 g h⁻¹. The concentration of ozone in both the inlet gas stream and the off-gas exiting from the reactor headspace was quantified by iodometric titration, following the method of Kruanak and Jarusutthirak (2019).

For lignin degradation experiments, the reactor was filled with 3.0 L of synthetic lignin solution prepared at initial concentrations of 50, 80, 100, and 150 mg L⁻¹. The solution pH was adjusted to 3, 5, 7, 9, or 11, and all experiments were

performed at ambient temperature (28-32°C). In catalytic ozonation experiments, ZnO-coated gravel catalyst (ZnO/gravel) was placed on a perforated tray within the reactor. The catalyst interacted simultaneously with the ozonated bubbles, ensuring continuous mixing. Catalyst dosages were varied at 1, 2, and 3 g L⁻¹, relative to the 3.0 L of lignin-containing wastewater. Samples (50 mL) were withdrawn at predetermined intervals up to 60 min for subsequent analysis of lignin decolorization and degradation.

Analytical Methods

Lignin concentration was quantified using a UV - Vis spectrophotometer (Hach DR6000, program 97, color ADMI, method 10048) with a 1-inch cuvette. Ozone concentrations from both the generator output and reactor off - gas were determined by iodometric titration following APHA (1998) guidelines.

Results and Discussion

Catalyst Characterization

Zinc oxide (ZnO) was successfully immobilized on gravel supports via a modified sol-gel method. Figure 2 showed that the XRD diffractogram displays distinct and intense peaks, reflecting the well-ordered crystalline nature of the synthesized material. Major reflections appear at approximately 2θ values of 31.8°, 34.4°, 36.3°, 47.5°, 56.6°, 62.9°, 66.4°, and 68.0°, which are assigned to the (100), (002), (101), (102), (110), (103), (200), and (112) planes, respectively. The pronounced intensity at the (101) plane indicates that this orientation is dominant within the crystal lattice. These diffraction signatures are in good agreement with the standard wurtzite hexagonal phase of ZnO (JCPDS 36-1451), confirming the successful formation of pure ZnO without noticeable secondary phases. The sharpness and narrow width of the peaks imply the presence of well-crystallized particles with relatively small crystallite dimensions. Moreover, the lack of additional diffraction lines associated with Zn(OH)₂ or *metallic* Zn suggests that the synthesis protocol yielded a phase-stable ZnO structure. The high peak intensity further reflects strong lattice ordering, demonstrating the effectiveness of the crystal growth process. Collectively, the XRD results verify that the obtained material is highly crystalline wurtzite ZnO, making it a promising candidate for applications that demand high structural quality, such as photocatalysis, adsorption processes, and electronic device development. The XRD pattern of the ZnO/gravel composite (Figure 2) confirmed the

formation of ZnO crystals, consistent with earlier reports (Hayat *et al.*, 2011; Zhao *et al.*, 2025). No extraneous peaks were observed, indicating the high purity of the ZnO phase. The XRD analysis revealed that ZnO crystallized in the hexagonal wurtzite structure with a polycrystalline nature, while high-resolution transmission electron microscopy (HR-TEM) indicated a particle size distribution of 32-37 nm.

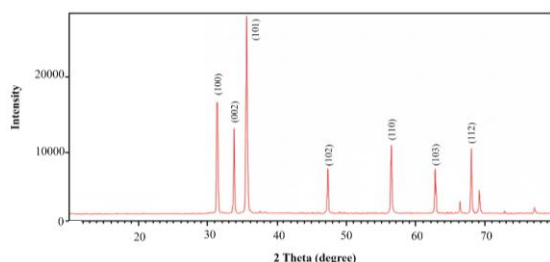


Figure 2. XRD pattern of ZnO catalysts prior to lignin degradation

Morphological characteristics were examined using SEM (Figure 3). SEM images showed distinct ZnO coatings on the gravel surface prior to lignin degradation (Figure 3a). After 60 min of ozonation with lignin solution, morphological changes were evident on the ZnO-coated surface (Figure 3b), while uncoated gravel was used as a control (Figure 3c).

XRF spectroscopy was employed to confirm ZnO immobilization. The Zn content of the catalyst was 0.207% (equivalent to 0.257% ZnO) after impregnation, verifying the successful loading of ZnO onto the gravel support (Table 1).

Effect of pH and Initial Lignin Concentration on Ozonation

The pH of the solution significantly influenced lignin degradation by ozonation, as it governs the generation of hydroxyl radicals ($\cdot\text{OH}$) (Nawrocki & Kasprzyk-Hordern, 2010; Jin *et al.*, 2023). Figure 4(a) - Figure 4(d) illustrate the removal efficiencies of lignin at initial concentrations of 50, 80, 100, and 150 mg L⁻¹ across different pH conditions.

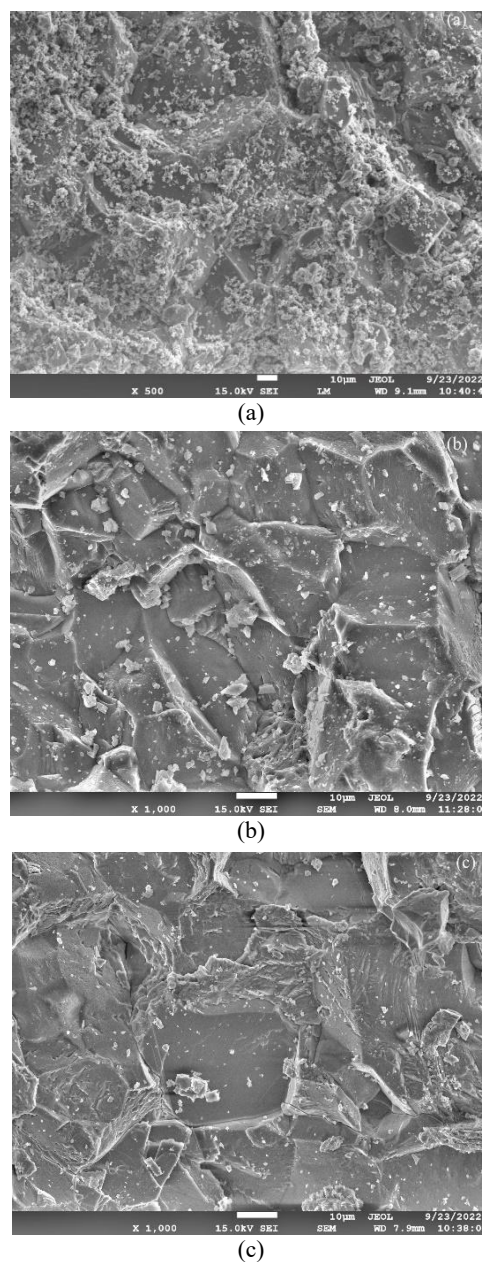


Figure 3. SEM micrographs: (a) ZnO/gravel before use, (b) ZnO/gravel after 60 min operation and (c) gravel control

Table 1. XRF analysis of pure gravel and ZnO/gravel catalysts

Formula	Mass (%)		Element	Mass (%)	
	pure	ZnO/Gravel		pure	ZnO/Gravel
CaO	99.26	97.370	Ca	70.94	69.592
ZnO	97.50	0.257	Zn	97.09	0.207
SiO ₂		1.759	Si		0.822
Cr ₂ O ₃		0.299	Cr		0.205
Br ₂ O		0.009	Br		0.009
PbO		0.302	Pb		0.281
			O		28.885
Norm.		100			100

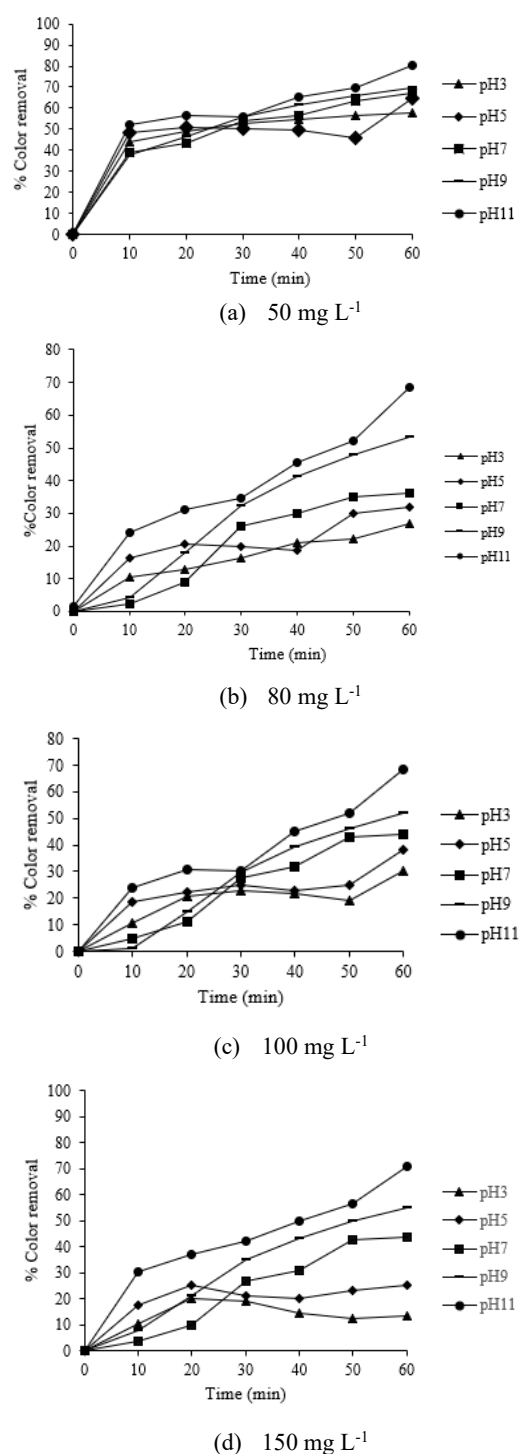


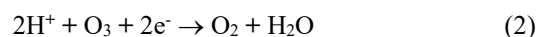
Figure 3. Lignin removal efficiencies by ozonation at different pH values and initial concentrations: (a) 50 mg L⁻¹, (b) 80 mg L⁻¹, (c) 100 mg L⁻¹, and (d) 150 mg L⁻¹

At 50 mg L⁻¹, lignin removal efficiencies after 60 min were 57.82%, 64.74%, 66.96%, 69.54%, and 80.07% at pH of 3, 5, 7, 9, and 11, respectively

(Figure 4a). At higher initial concentrations (80-150 mg L⁻¹), efficiencies decreased, reflecting competition between lignin molecules and hydroxyl radicals. Nevertheless, higher pH consistently enhanced removal efficiencies, reaching 71.00% at pH of 11 with 150 mg L⁻¹ lignin.

This phenomenon can be explained by the pH-dependent decomposition of ozone. Under acidic conditions, ozone reacts with H⁺ to form O₂ and H₂O (Equation 2). In alkaline media, ozone reacts with •OH, producing reactive radical species (Equations 3-5). Hydroxyl radicals exhibit much higher oxidation potential than molecular ozone, promoting faster and more extensive lignin degradation (Nawrocki & Kasprzyk-Hordern, 2010).

Acidic condition



Alkaline condition



Figure 4, illustrates the influence of initial solution pH on the percentage of color removal over 60 min. The removal efficiency increased progressively for all pH levels, indicating that reaction time is a critical parameter governing oxidative degradation. However, the extent of improvement varied markedly with pH. At highly alkaline conditions (pH of 11), the process exhibited the most rapid and efficient color reduction. The removal percentage increased steeply within the first 10 min and continued to rise steadily, reaching approximately 70% at 60 min. This suggests enhanced radical generation and improved interaction between the oxidizing agent and chromophoric compounds under alkaline conditions. At pH of 9, the system also demonstrated strong removal capability, with color removal gradually increasing to over 50% at the final reaction time. Although slightly lower than pH of 11, the performance remained significantly superior to acidic media. Neutral conditions (pH of 7) resulted in moderate performance. The removal efficiency rose gradually, achieving about 35-40% after 60 min. This indicates that the reaction can proceed under neutral conditions but less effectively compared to alkaline environments. Under weakly acidic conditions (pH of 5), color reduction was noticeably lower, reaching around

30% after 60 min. The slow increase in removal percentage suggests limited oxidative activity and possibly reduced interaction between reactive species and the pollutant. The lowest performance was observed at pH of 3, where color removal remained below 25% throughout the experiment. Strong acidity may suppress hydroxyl radical formation or hinder catalyst surface activity, resulting in poor degradation efficiency.

Following ozonation, solution pH decreased, attributed to the formation of organic acids (e.g., oxalic, acetic, formic acids) and the consumption of $\cdot\text{OH}$ during ozone decomposition and radical generation (Mvula *et al.*, 2009).

Overall, the results clearly indicate that alkaline conditions greatly enhance color removal, whereas acidic environments suppress the reaction. The trend follows:

$$\text{pH } 11 > \text{pH } 9 > \text{pH } 7 > \text{pH } 5 > \text{pH } 3$$

This behavior implies that the degradation mechanism is more favorable when hydroxyl radicals are more readily produced, which typically occurs at higher pH values. Thus, regulating pH provides a key strategy for maximizing treatment efficiency in color-contaminated wastewater.

Reaction Kinetics of Ozonation

The kinetics of lignin degradation by ozonation were evaluated using a first-order model (Equation 6). Apparent rate constants (k_{app}) were derived from the slopes of $\ln(C/C_0)$ versus time plots.

$$\ln C = \ln C_0 - k_{\text{app}} \cdot t \quad (6)$$

The results (Figure 5) demonstrated that k_{app} decreased with increasing initial lignin concentration (50–150 mg L⁻¹), due to the fixed ozone supply being insufficient to degrade higher pollutant loads. Conversely, higher pH values enhanced k_{app} , corroborating the role of $\cdot\text{OH}$ radicals generated under alkaline conditions.

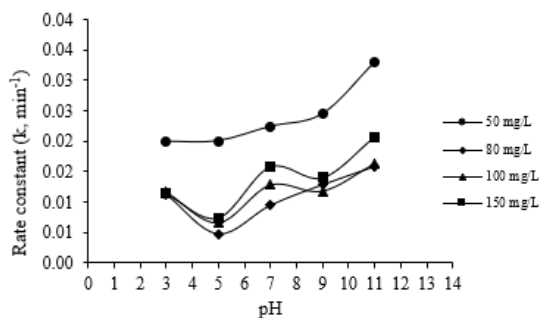
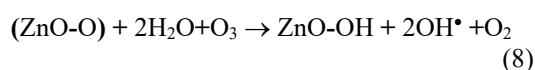
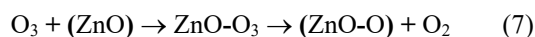


Figure 5. Apparent first-order rate constants for lignin degradation by ozonation

Effect of Initial Lignin Concentration on the Apparent Rate Constant. Figure 5 presents the apparent first-order rate constants (k) determined for lignin degradation under different initial concentrations during ozonation. The results indicate a clear inverse relationship between lignin concentration and the rate constant. At lower initial lignin levels, the ozonation process proceeds more rapidly, reflected by higher k values. This suggests that the oxidizing species generated during ozonation interact more efficiently with lignin molecules when the substrate concentration is low, allowing faster breakdown of chromophoric structures. As the initial lignin concentration increases, the rate constant gradually decreases. This reduction may be attributed to several factors: (i) increased competition among lignin molecules for available hydroxyl radicals and ozone molecules, (ii) radical scavenging by reaction intermediates, and (iii) accumulation of degradation by-products that may hinder mass transfer or active-site accessibility. High substrate concentration may also consume ozone more rapidly, leaving insufficient oxidants to sustain fast degradation kinetics. Overall, the trend demonstrates that ozonation performs more efficiently at lower lignin concentrations, whereas higher concentrations require longer treatment times to achieve comparable removal. These findings emphasize the importance of lignin loading in process design, indicating that pretreatment dilution or staged ozonation may enhance reaction performance in real wastewater applications.

Effect of ZnO Catalyst Dosage on Catalytic Ozonation

Catalytic ozonation experiments were conducted at an initial lignin concentration of 100 mg L⁻¹ and pH of 11 with ZnO/gravel dosages of 0, 1, 2, and 3 g L⁻¹. As shown in Figure 6, lignin removal efficiency at 60 min increased from 51.75% (ozonation alone) to 88.81% with 1 g L⁻¹ catalyst. Further increases to 91.43% and 94.88% were achieved with 2 and 3 g L⁻¹, respectively. The enhanced degradation was attributed to the availability of additional active sites facilitating ozone decomposition and $\cdot\text{OH}$ generation (Equations 7–8).



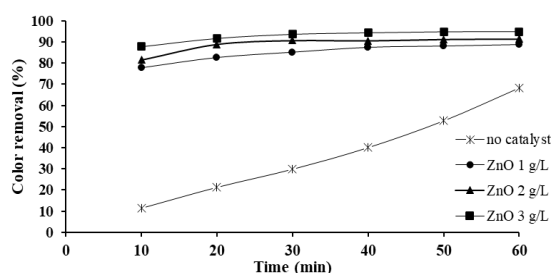


Figure 6. Effect of ZnO/ gravel dosage on lignin removal efficiency

Figure 6 shows the influence of ZnO/gravel dosage on lignin removal performance during the treatment process. The results indicate that the removal efficiency increases progressively with increasing catalyst dosage up to an optimal level. At lower ZnO/gravel dosages, the number of active catalytic sites is limited, resulting in relatively low degradation efficiency and slower breakdown of lignin molecules. As the dosage increases, the system provides more surface area and reactive sites for ozone interaction, thereby enhancing the formation of reactive oxygen species (ROS), such as hydroxyl radicals, which are responsible for attacking lignin's aromatic structure. However, when the ZnO/gravel dosage exceeds the optimal range, the improvement in removal efficiency becomes less significant or may even decline slightly. This behavior is likely attributed to catalyst agglomeration or excessive suspension density, which may reduce light penetration, active site accessibility, or mass transfer efficiency. Additionally, excessive solid dosage can lead to increased radical quenching, resulting in less effective oxidizing species available for lignin degradation. Overall, the findings suggest that lignin removal efficiency is strongly dependent on catalyst loading, where enough ZnO/gravel is necessary to maximize oxidation activity. The identification of an optimal dosage is therefore essential to balance catalytic surface availability with mass transfer efficiency, ultimately contributing to cost-effective ozonation treatment for lignin-containing wastewater.

However, efficiencies plateaued beyond 3 g L⁻¹, possibly due to limited ozone supply and self-quenching of $\cdot\text{OH}$ radicals (Equation 9).



Kinetic analysis (Figure 7) confirmed first-order behavior, with k_{app} increasing alongside catalyst dosage. One-way ANOVA revealed no significant differences ($p > 0.05$) among dosages 1,

2 and 3 g L⁻¹, suggesting 3 g L⁻¹ as the optimum catalyst loading.

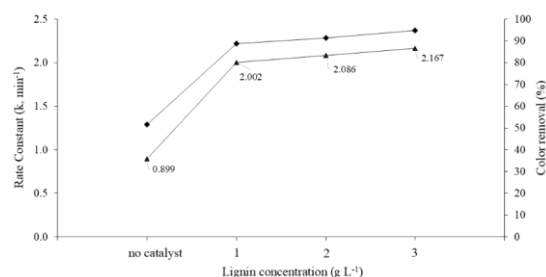


Figure 7. Apparent rate constants for lignin degradation by catalytic ozonation on different ZnO dosage

Figure 7 show that increasing the initial lignin concentration under catalytic ozonation markedly enhanced both the apparent rate constant (k) and color removal, with values rising from 0.899 min⁻¹ in the non-catalyzed system to approximately 2.002-2.167 min⁻¹ when lignin increased from 1 to 3 g L⁻¹. The sharp improvement observed between the control and the catalytic condition confirms that ZnO effectively accelerates the oxidation of lignin, most likely through surface-mediated ozone decomposition and subsequent hydroxyl radical generation. However, the slight increase in k beyond 1 g L⁻¹ suggests that catalytic performance approaches saturation at higher substrate levels, indicating possible limitations associated with active site availability or diffusion. Overall, catalytic ozonation with ZnO significantly improves reaction kinetics and color removal efficiency compared to ozonation alone, demonstrating strong potential for treating lignin-rich wastewater while also highlighting that increasing concentration beyond a particular threshold yield diminishing kinetic benefits. These results demonstrate that the presence of the ZnO catalyst significantly enhances the kinetics and performance of lignin removal compared to ozonation alone. The marked increase in rate constant (roughly a two- to three-fold enhancement) is consistent with prior studies of heterogeneous catalytic ozonation. For instance, studies using nano-ZnO as a catalyst for the degradation of organic pollutants such as pesticide analogues showed a fourfold increase in rate constant compared to non-catalytic ozonation (Yuan *et al.*, 2017). The plateau in k beyond 1 g L⁻¹ lignin suggests that further increasing the lignin concentration exerts diminishing returns on reaction kinetics. This behavior may be explained by

saturation of the catalyst surface and/or limitation in mass transfer: as lignin concentration rises, active sites on ZnO become increasingly occupied, limiting additional increase in reactive radical generation or ozone decomposition - thereby constraining further acceleration of the reaction. A similar trend has been reported in catalytic ozonation studies of other refractory organics, where beyond a certain pollutant concentration, the increase in rate constant levels off. Mechanistically, the enhancement achieved by ZnO likely arises from accelerated decomposition of ozone at the catalyst surface, producing reactive species such as hydroxyl radicals ($\cdot\text{OH}$), which drive the rapid oxidation of lignin. This interpretation aligns with commonly accepted mechanisms in heterogeneous catalytic ozonation systems. In summary, the data strongly supports that catalytic ozonation with ZnO significantly enhances both the rate and the effectiveness of lignin degradation (and color removal), but that the benefits level off at higher lignin concentrations due to likely surface saturation and mass-transfer limitations. These findings are consistent with the broader body of literature on catalytic ozonation, demonstrating the potential of ZnO-based heterogeneous catalysts for advanced treatment of lignin-rich wastewater.

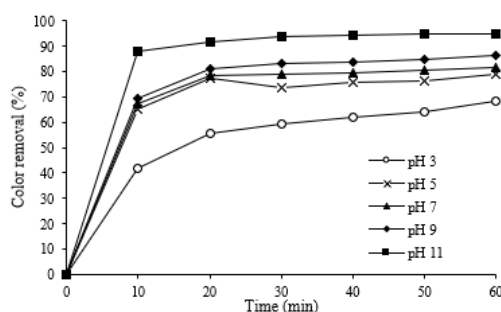


Figure 8. Effect of pH on lignin degradation by catalytic ozonation

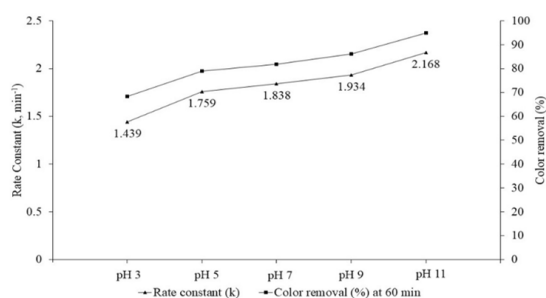


Figure 9. Apparent rate constants of catalytic ozonation at different pH values

Effect of pH on Catalytic Ozonation

The effect of pH on catalytic ozonation was evaluated at 100 mg L⁻¹ lignin and 3 g L⁻¹ ZnO/gravel. Removal efficiencies after 60 min increased from 68.25% at pH of 3 to 78.87% (pH of 5), 86.16% (pH of 9), and 94.90% (pH of 11) (Figure 8). Reaction rate constants similarly increased with pH (Figure 9).

Unlike ozonation alone, catalytic ozonation effectively generated $\cdot\text{OH}$ radicals across a broad pH range (3-11), confirming that ZnO facilitates radical generation independent of alkalinity. This behavior is consistent with previous reports (Amutha *et al.*, 2014).

The influence of pH on catalytic ozonation performance is demonstrated in Figure 9, where an increase in pH from 3 to 11 results in a steady rise in the apparent rate constant from approximately 1.439 to 2.168 min⁻¹, accompanied by greater color removal at 60 minutes, confirming that alkaline conditions markedly enhance reaction kinetics and treatment efficiency. This improvement is typically attributed to the enhanced formation of hydroxyl radicals ($\cdot\text{OH}$) from ozone decomposition in basic media, which accelerates the degradation of chromophoric structures and aligns with previous reports indicating increased color and COD removal at elevated pH. Under acidic conditions, ozone predominantly reacts through the direct molecular pathway, often yielding slower decolorization, whereas at higher pH, hydroxide ions promote rapid catalytic ozone decomposition and extensive $\cdot\text{OH}$ radical generation capable of attacking a broader range of aromatic compounds. The sustained increase in both k and color removal up to pH of 11, without evidence of decline, may relate to catalyst surface properties - particularly when the point-of-zero-charge (PZC) is lower than the system pH - resulting in a negatively charged surface that enhances pollutant interaction, radical formation, and overall ozonation efficiency. Therefore, alkaline pH demonstrates the most favorable conditions for catalytic degradation of lignin-derived color or similar chromophoric contaminants, although practical considerations such as post-treatment pH adjustment and corrosion control remain important for full-scale application.

Conclusion

A ZnO/gravel catalyst was successfully synthesized using a sol-gel impregnation method, achieving ZnO loading of 0.257% on the gravel support. The catalyst demonstrated high stability and effective enhancement of ozonation for lignin degradation.

Key operational parameters influencing performance were initial lignin concentration, solution pH, and reaction time.

Ozonation without a catalyst achieved a maximum lignin removal efficiency of 43.38% at an initial concentration of 100 mg L⁻¹, pH 3, and a hydraulic retention time of 60 min. The reaction followed first - order reaction kinetics with rate constants of 0.0117 min⁻¹ at pH 3 and 0.899 min⁻¹ at pH 11. Increasing the pH to 11 enhanced lignin removal to 51.75%. Catalytic ozonation (ZnO/gravel) significantly improved degradation efficiency, reaching 94.90% lignin removal at 100 mg L⁻¹, pH of 11, 3 g L⁻¹ catalyst dosage, and 60 min reaction time. The apparent rate constant (2.168 min⁻¹) was markedly higher than ozonation alone (0.899 min⁻¹). Importantly, catalytic ozonation achieved consistent efficiencies (78.87-94.90%) across a wide pH range (5-11). The ZnO/gravel catalyst exhibited reusability with minimal efficiency loss, and residual Zn concentrations in treated effluents remained below regulatory discharge limits (<1 mg L⁻¹). These findings confirm that catalytic ozonation with ZnO/gravel is a promising advanced oxidation process for the treatment of lignin-containing wastewater.

Acknowledgement

This research was financially supported by the Science, Research and Innovation Promotion Fund (Fundamental Fund, Fiscal Year 2023) through Khon Kaen University under Research No. 179566, together with the Graduate Research Fund of Khon Kaen University for the academic year 2020.

References

- Amutha, R., Sillanpää, M., Lee, G. J., Lin, J. C., Yang, C. K., & Wu, J. J. (2014). Catalytic ozonation of 2-ethoxyethyl acetate using mesoporous nickel oxalates. *Catalysis Communications*, 43, 88-92. <https://doi.org/10.1016/j.catcom.2013.09.009>
- APHA, AWWA, & WEF. (1998). *Standard methods for the examination of water and wastewater* (20th ed.). American Public Health Association.
- Bashiri, H., & Rafice, M. (2014). Kinetic Monte Carlo simulation of 2,4,6-trichlorophenol ozonation in the presence of ZnO nanocatalyst. *Journal of Saudi Chemical Society*, 20, 474-479. <https://doi.org/10.1016/j.jscs.2014.11.001>
- Boczkaj, G., & Fernandes, A. (2017). Wastewater treatment by means of advanced oxidation processes at basic pH conditions: A review. *Chemical Engineering Journal*, 320, 608-633. <https://doi.org/10.1016/j.cej.2017.03.084>
- Dong, C., Fang, W., Yi, Q., & Zhang, J. (2022). A comprehensive review on reactive oxygen species (ROS) in advanced oxidation processes (AOPs). *Chemosphere*, 308, Article 136205. <https://doi.org/10.1016/j.chemosphere.2022.136205>
- Fisher, A. B., & Fong, S. S. (2014). Lignin biodegradation and industrial implications. *AIMS Bioengineering*, 1(2), 92-112. <https://doi.org/10.3934/bioeng.2014.2.92>
- Fu, S., Dong, S., Cao, T., Cui, B., Jiang, J., Sun, H., Zhang, C., & Zhou, D. (2024). The transition metal composition could promote α -Fe₂O₃ catalytic ozonation at mild conditions by improving electron transfer. *Journal of Cleaner Production*, 477, 143896. <https://doi.org/10.1016/j.jclepro.2024.143896>
- Ghughe, S. P., & Saroha, A. K. (2018). Catalytic ozonation for the treatment of synthetic and industrial effluents-Application of mesoporous materials: A review. *Journal of Environmental Management*, 211, 83-102. <https://doi.org/10.1016/j.jenvman.2018.01.052>
- Hayat, K., Gondal, M. A., Khaled, M. M., Ahmed, S., & Shems, A. M. (2011). Nano ZnO synthesis by modified sol gel method and its application in heterogeneous photocatalytic removal of phenol from water. *Applied Catalysis A: General*, 393(1-2), 122-129. <https://doi.org/10.1016/j.apcata.2010.11.032>
- Jin, X., Wu, C., Fu, L., Tian, X., Wang, P., & Zhou, Y. (2023). Development, dilemma and potential strategies for the application of nanocatalysts in wastewater catalytic ozonation: A review. *Journal of Environmental Sciences*, 124, 330-349. <https://doi.org/10.1016/j.jes.2021.09.041>
- Kruanak, K., & Jarusutthirak, C. (2019). Degradation of 2,4,6-trichlorophenol in synthetic wastewater by catalytic ozonation using alumina supported nickel oxides. *Journal of Environmental Chemical Engineering*, 7, 102825. <https://doi.org/10.1016/j.jece.2018.102825>
- Mvula, E., Naumov, S., & von Sonntag, C. (2009). Ozonolysis of lignin models in aqueous solution: Anisole, 1,2-dimethoxybenzene, 1,4-dimethoxybenzene, and 1,3,5-trimethoxybenzene. *Environmental Science & Technology*, 43(16), 6275-6282. <https://doi.org/10.1021/es900803p>
- Nawrocki, J., & Kasprzyk-Hordern, B. (2010). The efficiency and mechanisms of catalytic ozonation. *Applied Catalysis B: Environmental*, 99, 27-42. <https://doi.org/10.1016/j.apcatb.2010.06.033>
- Wei, W., Tang, Z., Zhou, Z., Zuo, L., Wang, Z., Li, L., & Yang, Y. (2025). ZnO-doped lignin-based carbon as a catalyst for ciprofloxacin photocatalytic degradation. *International Journal of Biological Macromolecules*, 305, Article 141049. <https://doi.org/10.1016/j.ijbiomac.2025.141049>
- Yang, Q., Wei, J., Chen, Y., Xu, Z., Ma, D., Zheng, M., & Li, J. (2024). Continuous operation of nano-catalytic ozonation using membrane separation coupling system: Influence factors and mechanism. *Chemosphere*, 362, Article 142117. <https://doi.org/10.1016/j.chemosphere.2024.142117>
- Yuan, X., Yan, X., Xu, H., Li, D., Sun, L., Cao, G., & Xia, D. (2017). Enhanced ozonation degradation of atrazine in the presence of nano-ZnO: Performance, kinetics and effects. *Journal of Environmental Sciences*, 61, 3-13. <https://doi.org/10.1016/j.jes.2017.04.037>
- Zhao, R., Zong, S., Qingfu, M. Q., Xu, Z., & Yuan, J. (2025). Investigating the electrocatalytic properties of ZnO-based composite membrane for dye removal. *Scientific Reports*, 15, 6306. <https://doi.org/10.1038/s41598-024-75153-2>
- Zhu, C., & Wang, X. (2025). Nanomaterial ZnO synthesis and its photocatalytic applications: A review. *Nanomaterials*, 15(9), Article 682. <https://doi.org/10.3390/nano15090682>