

Catalytic Ozonation with ZnO Nanoparticles: A Novel Approach to Lignin Degradation in Synthetic Wastewater

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ABSTRACT

The purpose of this study is to evaluate ZnO nanoparticle-catalyzed ozonation degradation lignin in synthetic wastewater. By applying response surface methodology (RSM) and central composite design (CCD), we analyzed the interaction between key factors and optimized their conditions. pH, ZnO dose, time, and lignin concentration were varied and encoded into a second-order model, with ANOVA confirming its significance (F -value=19.53). The model predicted a 99.99% lignin degradation efficiency under optimal conditions: pH 11, 1.0 g ZnO, 50 minutes, and 50 mg/L lignin. The high correlation ($R^2=0.9480$) validated the model, highlighting the effectiveness of ZnO nanoparticle-catalyzed ozonation for lignin removal.

HIGHLIGHTS

This study used response surface methodology (RSM) with central composite design (CCD) to optimize key factors in the catalytic ozonation process with ZnO nanoparticles. The effects of pH, ZnO dosage, time, and lignin concentration on lignin decolorization were evaluated, with pH and catalyst dosage found to be the most influential factors.

1. INTRODUCTION

Ozone is increasingly used in wastewater treatment for organic contaminants, breaking bonds through two mechanisms: direct reaction with organic substances via electrophilic or cyclo-dipolar addition (direct ozone) and indirect reaction via free radicals like hydroxyl, superoxide, and hydrogen peroxy radicals. These reactions reduce large polymer molecules or break double/triple bonds into single ones. The global pulp and paper sector generates more than fifty million tons of lignin each year, a thick black liquid that can't be directly released into water (Haqa et al., 2020; Kumar et al., 2021). Lignin is a complex polymer made of carbon-carbon bonds, with components like thiol, sulfide, and phenolic groups (hydroxyl, methoxy, carboxylic, and carbonyl). Derived from monolignols, lignin exhibits biological activities such as antioxidant and antimicrobial properties, which vary based on plant source.

Many researchers have developed advanced oxidation processes (AOPs) for lignin wastewater

treatment to manage large organic compounds by breaking double bonds and reducing color (Zhou et al., 2023). AOPs, which generate hydroxyl radicals ($\cdot\text{OH}$), efficiently degrade pollutants by reacting with functional groups, double bonds, and aromatic carbons (Einaga et al., 2024; Nawrocki and Kasprzyk-Hordern, 2010). The catalytic ozone process (COP), an effective AOP for degrading organic matter and lignin, involves metal oxide catalysts reacting with ozone to produce superoxide radicals, which generate hydroxyl radicals ($\cdot\text{OH}$) that non-selectively degrade organic matter (Mao et al., 2025). COP enhances ozone efficiency, reduces by-products, and lowers treatment costs by accelerating oxidation and reducing contact time (Einaga et al., 2024). Common catalysts include TiO_2 , MnO_2 , Al_2O_3 , CuO , MgO , and others, which boost radical generation and reaction rates (Li et al., 2023; Mohammadi et al., 2016).

The effectiveness of catalytic ozonation depends on several factors, including the pH of the solution, pollutant type, catalyst amount, ozone

exposure time, and pollutant concentration. Catalytic ozonation is divided into homogeneous and heterogeneous types, the heterogeneous ozonation being a new AOP that enhances ozone generation in the presence of effective hydroxyl radical scavenging catalysts. COP is an economical wastewater treatment method because of its catalyst recoverability and low secondary contamination. Its catalytic mechanisms enhance free radical generation, facilitate singlet oxygen release, and improve the adsorption of ozone and organic molecules on the catalyst surface.

Zinc oxide (ZnO) is a cost-effective, non-toxic, and ecologically benign heterogeneous catalyst capable of degrading diverse organic pollutants, frequently employed in wastewater treatment. A primary application is ozone decomposition, originally utilized for oxidizing various organic compounds in the liquid phase. The well-developed surface, a characteristic feature of nanomaterials, plays a significant role in advancing catalysis. The reduction in average particle size and the corresponding increase in specific surface area enhance the number of active sites available for reactions. A limited number of publications have explored the use of ZnO catalyst for ozone decomposition and the removal of organic pollutants. However, other authors have not studied the use of zinc oxide as a catalyst in combination with ozone for lignin degradation.

2. METHODOLOGY

2.1 Materials

Stock solution containing soda lignin (Lignin Alkaline, Molecular Formula $C_{30}H_{25}SO_4$) Cas. No. 8068-05-1 (Tokyo Chemical Industry Co., LTD) at 1,000 mg/L. ZnO powder particle size 25 nm (XRD analysis) obtained from the Agricultural Nano Research Center, King Mongkut's University of Technology Thonburi, sodium hydroxide (AR grade, Ajax Finechem, Australia) at 0.01 M adjusted for pH level each condition and nitric acid (AR grade, Ajax Finechem, Australia) at 0.01 M.

Catalyst preparation and characterization; zinc oxide (ZnO) nanopowder (25-50 nm) supplied by the Agricultural Nanotechnology Center, King Mongkut's Institute of Technology, 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 $104 \pm 1^\circ\text{C}$ 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), 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 (EDS). These analyses were performed to confirm the presence, distribution, and stability of ZnO on the gravel substrates for subsequent lignin decolorization experiments.

2.2 Experimental apparatus and procedure

Ozonation experiment included an oxygen gas generator, ozone generator (Biozone ozone generator 5 g/h, MMS Engineering Co. Ltd. Thailand) for production of ozone. The ozone flow rate was 7.0 L/min (ozone production was 23.4 mg O_3 /min, [Figure 1](#)). The laboratory scale ozone batch reactor is borosilicate glass 1.0 L (inner diameter 0.16 m, height 0.50 m). The ozone gas concentration at the outlet was measured using an ozone trap reactor containing 50 mL of acidified 2.0% KI solution for determination of unreacted ozone. [Table 1](#) presents the average characteristics of the influent wastewater. The concentration of ozone in the gas was measured by the iodometric titration method. The experimental setup utilized a 1.0 L bottle containing of 50, 100, and 150 ppm lignin synthetic solution. Each trial conducted in a batch setup over a 60-minute period. At the end of each trial, 30 mL of samples were collected through a tube with an installed valve at the bottom of the bottle, stored at 4°C , and analyzed on the same day as the treatment. The experiments were performed at room temperature ($30 \pm 1^\circ\text{C}$) in 1.0 L of lignin synthetic wastewater solution under batch condition. The bottom of the reactor was equipped with gas diffusers to produce fine ozone bubbles. The parameters

influencing lignin degradation include solution pH, ZnO dosage, ozone exposure time, and initial lignin concentration. Samples were taken at specified reaction times to determine the residual lignin concentration. The lignin degradation rate was calculated by using Equation 2, where C_t is the lignin

concentration at a given time (t), and C_0 is the initial lignin concentration.

$$\text{Degradation rate (\%)} = \frac{(C_0 - C_t) \times 100}{C_0} \quad (2)$$

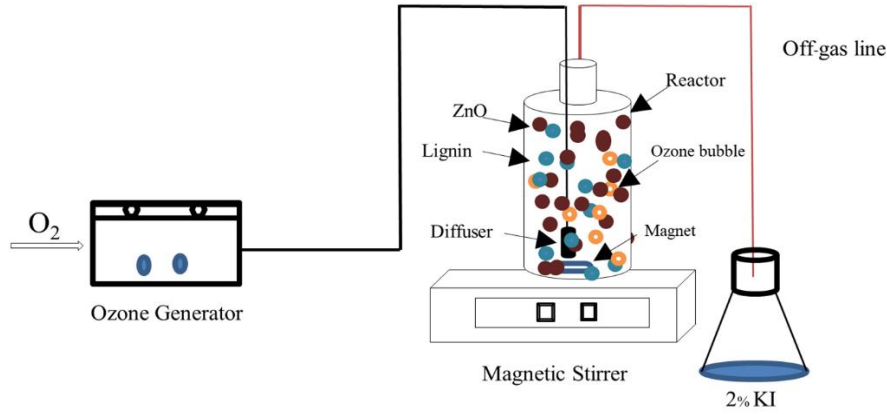


Figure 1. Schematic diagram of lignin degradation in a catalytic ozonation (ZnO) batch reactor

2.3 Analytical methods

Lignin degradation refers to the color concentration analyzed using a spectrophotometer (DR6000, Hach) following the ADMI method, and pH solution measured by Knick 761 pH-Meter Calimatic.

2.4 Experimental design

This study employed a factorial Central Composite Design (CCD) with four levels and a full CCD with three levels, guided by RSM (Hanapi et al., 2021). A total of thirty experimental evaluations were used, consisting of eight axis points, sixteen factorial points, and six center points. These experiments were designed to optimize key variables: pH, ZnO dosage, time, and initial lignin concentration. The experimental parameters and levels used CCD for this study were determined and shown in Table 1.

Optimization of the process involves calculating coefficients, predicting responses, and

verifying the developed model. The response expressed using Equation 3:

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{j=1}^n \beta_{ii} X_i^2 + \sum_{i=j}^{n-1} \sum_{i=j+1}^n \beta_{ij} X_i X_j + E \quad (3)$$

Where; Y is the response (removal efficiency, %); β_0 represents the regression coefficient; β_i , β_{ii} , and β_{ij} correspond to the linear, quadratic, and interaction coefficients; X_i and X_j correspond to the coded values independent process factors, and E is the experimental or residual error. Equation 3 shows the correlation between independent variables in coded values and predicted response based on Tables 1 and 2.

In addition, ANOVA analysis was used to assess the significance of the quadratic regression model using p -values at the 95% confidence level. Coefficient parameters were RSM analyzed using Minitab 19.

Table 1. Parameters, symbol, and coded values used in the CCD for lignin degradation using ZnO catalysis ozonation.

Parameters	Symbol	Actual and coded values		
		-1	0	+1
pH	A	5	8	11
ZnO dose (mg/L)	B	1	2	3
Ozonation time (min)	C	1	30	60
Lignin concentration (mg/L)	D	50	100	150

Table 2. Experimental design of lignin degradation experiment

Run	A	B	C	D	Efficiency (%)	
					Experiment	Predicted
1	8	2	0	100	0.10	22.42
2	8	4	27.5	100	83.15	74.81
3	8	2	27.5	0	99.99	93.59
4	8	2	72.5	100	72.00	91.88
5	8	2	27.5	100	69.30	71.17
6	8	2	27.5	100	72.00	71.17
7	2	2	27.5	100	50.00	31.29
8	8	2	27.5	200	69.00	72.27
9	8	0	27.5	100	45.80	51.00
10	14	2	27.5	100	7.72	23.30
11	8	2	27.5	100	67.30	71.17
12	5	1	5.0	150	5.41	18.54
13	8	2	27.5	100	73.00	71.17
14	8	2	27.5	100	72.80	71.17
15	5	3	50.0	50	90.50	93.18
16	5	3	5.0	50	20.27	31.18
17	5	1	5.0	50	8.98	21.45
18	11	3	5.0	150	25.00	32.54
19	11	1	5.0	150	15.40	9.25
20	11	3	5.0	50	23.00	30.69
21	11	1	5.0	50	10.00	10.65
22	5	3	50.0	150	65.00	73.25
23	5	3	5.0	150	24.00	31.52
24	11	1	50.0	50	94.64	83.65
25	11	3	50.0	50	98.70	94.47
26	5	1	50.0	50	91.30	92.66
27	11	1	50.0	150	64.00	61.99
28	5	1	50.0	150	80.64	69.49
29	8	2	27.5	100	70.30	71.17
30	11	3	50.0	150	90.00	76.06

3. RESULTS AND DISCUSSION

3.1 Catalyst characterization

Zinc oxide (ZnO) was successfully immobilized on gravel supports via a modified sol-gel method. 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.

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

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 3).

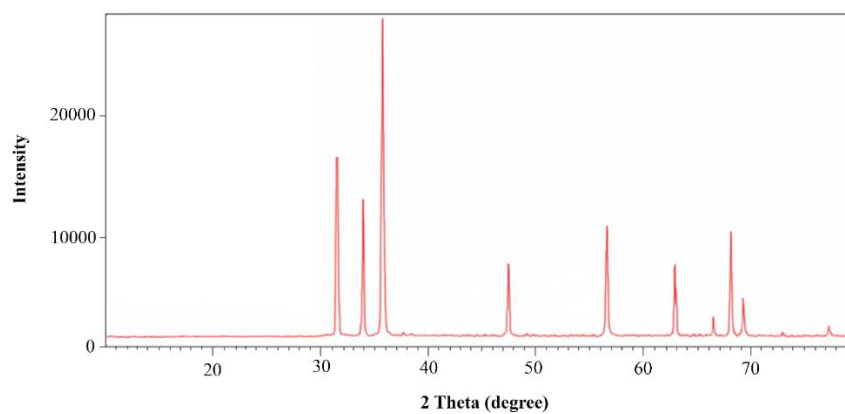


Figure 2. XRD pattern of ZnO catalysts prior to lignin degradation

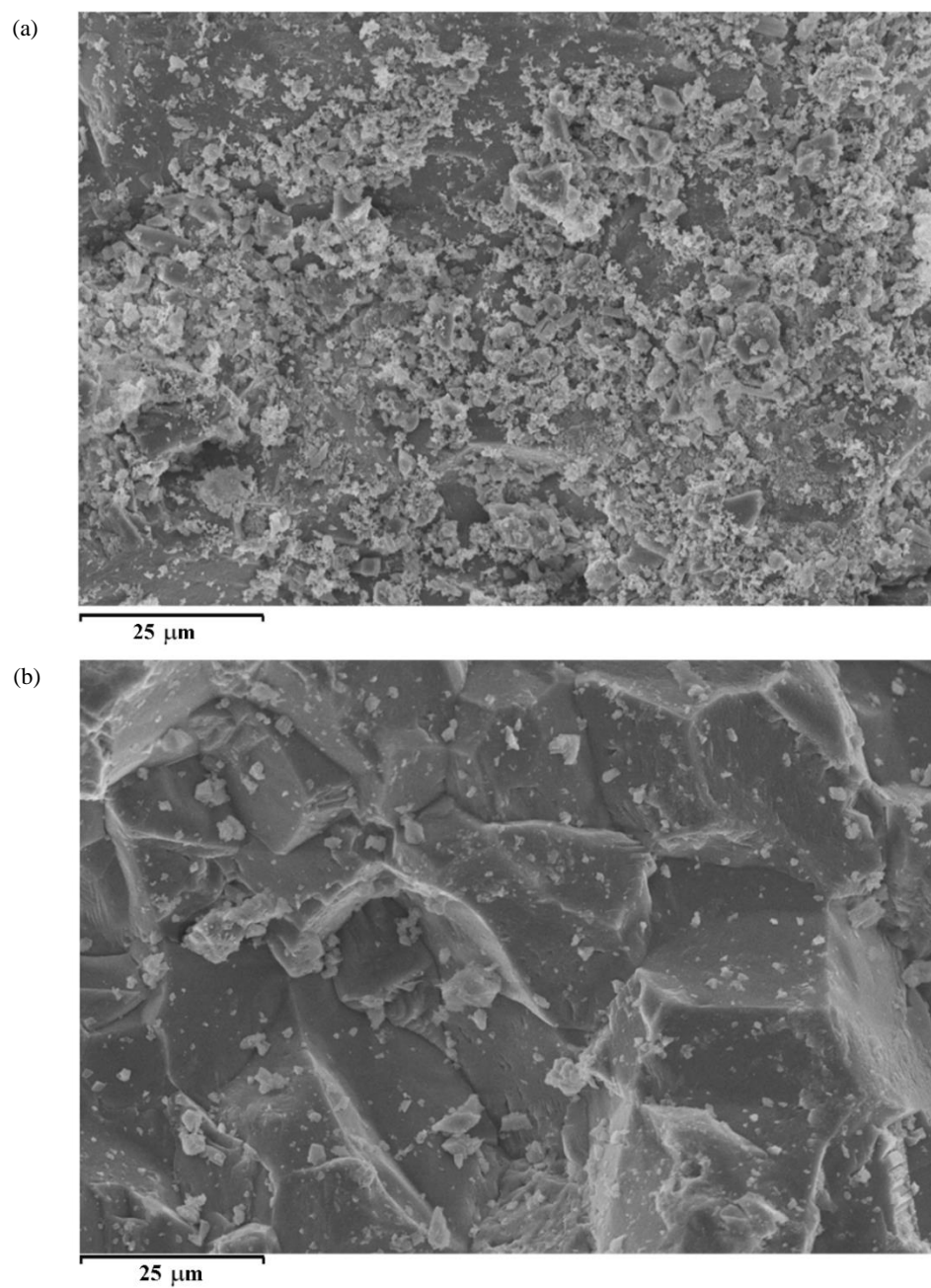


Figure 3. SEM micrographs: (a) ZnO/gravel before use, (b) ZnO/gravel after 60 min operation, and (c) gravel control

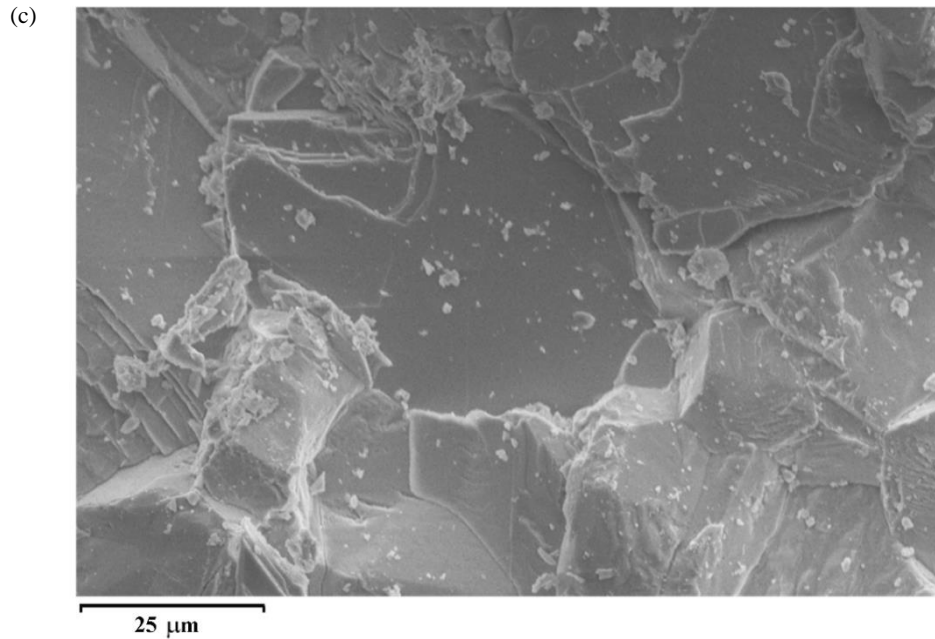


Figure 3. SEM micrographs: (a) ZnO/gravel before use, (b) ZnO/gravel after 60 min operation, and (c) gravel control (cont.)

Table 3. 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

3.2 Statistical analysis

3.2.1 CCD model fitting

The optimal conditions for lignin degradation in COP were identified using CCD within the framework of RSM and we are represented by the following Equation 4:

$$Y(\text{lignin degradation}) = -40.7 + 14.14A + 2.8B + 3.787C - 3.385D \quad (4) \\ + 0.859AB + 0.0066AC + 0.0025AD \\ - 0.102BC + 0.0163BD - 0.0045CD - 1.060A^2 \\ - 0.64B^2 - 0.0305C^2 + 0.002D^2$$

Where; A is pH, B is the amount of ZnO, C is the ozonation time, and D is the initial lignin concentration. The quality of the model is expressed as R^2 . The acceptability of the RSM model was confirmed by using analysis of variance (ANOVA), a statistical method that serves as an exploratory tool to

interpret observations and test hypotheses about the model parameters (shown in Table 4).

F value used to evaluate second-order regression. An F value of 18.62 for the quadratic model confirms its significance. Additionally, a “Prob>F” value less than 0.05 is statistically significant at the 95% confidence level. Larger F-values and smaller p-values highlight the significant effects of the corresponding coefficients. The results show that the regressions for lignin degradation are statistically significant, with $p\text{-values} < 0.05$ and large F values. According to the ANOVA table for the catalytic ozonation process, linear model terms (pH, dose, time, and initial lignin concentration) and the interaction term (B*D) were significant ($p < 0.05$), however the interaction terms are not significant. The experiment error because of using the lack of fit (LOF), with a p-value 0.004 confirmed

model significance. The LOF Of F value 0.004 suggests that the result is significant compared to pure error, with a 68.13% chance this outcome occurred due to noise. A non-significant LOF indicates a good model fit. The closer the R^2 value is near one that the better to the fit, with the predicted R^2 value of 0.9456, in good agreement with the adjusted R^2 value (0.8948). The optimum signal to noise ratio from the study is 14.608 (Adeq Precision). Thus, the quadratic model can be used to optimize operational parameters. [Figure 4](#)

shows the model aligns with the ANOVA results, and residual plots indicate a standard distribution, supporting the significance of terms like pH, dose, ozonation time, initial lignin concentration, and BD. Non-significant terms include AB, AC, AD, BC, and CD. A normal probability plot close to a straight line confirms a good model fit, validating the regression models for calculating lignin degradation under the given conditions responding by [Hanapi et al. \(2021\)](#).

Table 4. Analysis of variance (ANOVA) for lignin degradation (%)

Source	Sum of squares	F-value	p-value Prob>F
Model	29,027.6	18.62	< 0.0001
A	95.7	0.86	0.369
B	849.7	7.63	0.015*
C	22,779.7	204.54	0.000*
D	681.8	6.12	0.026*
A*B	106.2	0.95	0.344
A*C	3.2	0.03	0.868
A*D	2.3	0.02	0.888
B*C	84.9	0.76	0.396
B*D	10.6	0.09	0.762
C*D	410.7	3.69	0.074
A ²	2,537.0	22.78	0.000*
B ²	11.3	0.10	0.755
C ²	4,104.4	36.85	0.000
D ²	532.0	4.78	0.045*

Lack of fit values=1,645.6; R^2 =0.9456 (*p-Value indicates that model is significant)

3.3 The effects of catalytic ozonation ZnO different parameters on lignin degradation

3.3.1 Effect of initial pH

The pH (A) and ZnO dosage (B) on lignin degradation use ZnO nanoparticle ozone catalysis, while ozone time (C) and lignin concentration (D) were constant at intermediate level (C=27.5 min, D=100 mg/L) and shown in [Figure 4\(a\)](#). When pH and ZnO content increased, the lignin degradation efficiency continued to increase. The initial pH was 8, and using more than 2 g of ZnO nanoparticles, the degradation efficiency >70% achieved, as shown in [Figure 4\(a\)](#). The lignin degradation rate increased with the simultaneous rise in pH and ozonation time. Specifically, when pH values exceeded 11, and ozonation time surpassed 40 min, further increases in each of these variables individually boosted removal efficiency. In alkaline conditions with ozone exposure time of 50 min, the lignin degradation efficiency was more than 80% as shown in [Figure 4\(b\)](#). Moreover, [Figure 4\(c\)](#) indicates that the maximum lignin degradation occurred at a high

pH (pH=11), and the lowest lignin (10 mg/L) in fixed conditions achieved with an operating time of 27.5 min and a ZnO 3 g. In contrast, lignin degradation decreased as lignin concentration increased.

The pH solution influences the form in which lignin molecules exist, the decomposition of ozone and interactions with hydroxyl group on ZnO catalyst surface. It is well established that ozone resonance reacts preferentially with functional group complexes (OCH_3) and $\text{C}=\text{C}$ bond of aromatic in acidic conditions through selective reactions. On the contrary, in alkaline conditions, ozone molecules decompose to produce hydroxyl radicals, superoxide radicals, and hydrogen superoxide radicals, which are substances whose oxidizing power reacts non-selectively with organic substances, thus, together with the catalyst, promoting the formation of more hydroxyl radicals, which are beneficial for the decomposition of conjugated double bonds, functional groups of organic substances with complex lignin structures ([Amini et al., 2023](#); [Norabadi et al., 2020](#)).

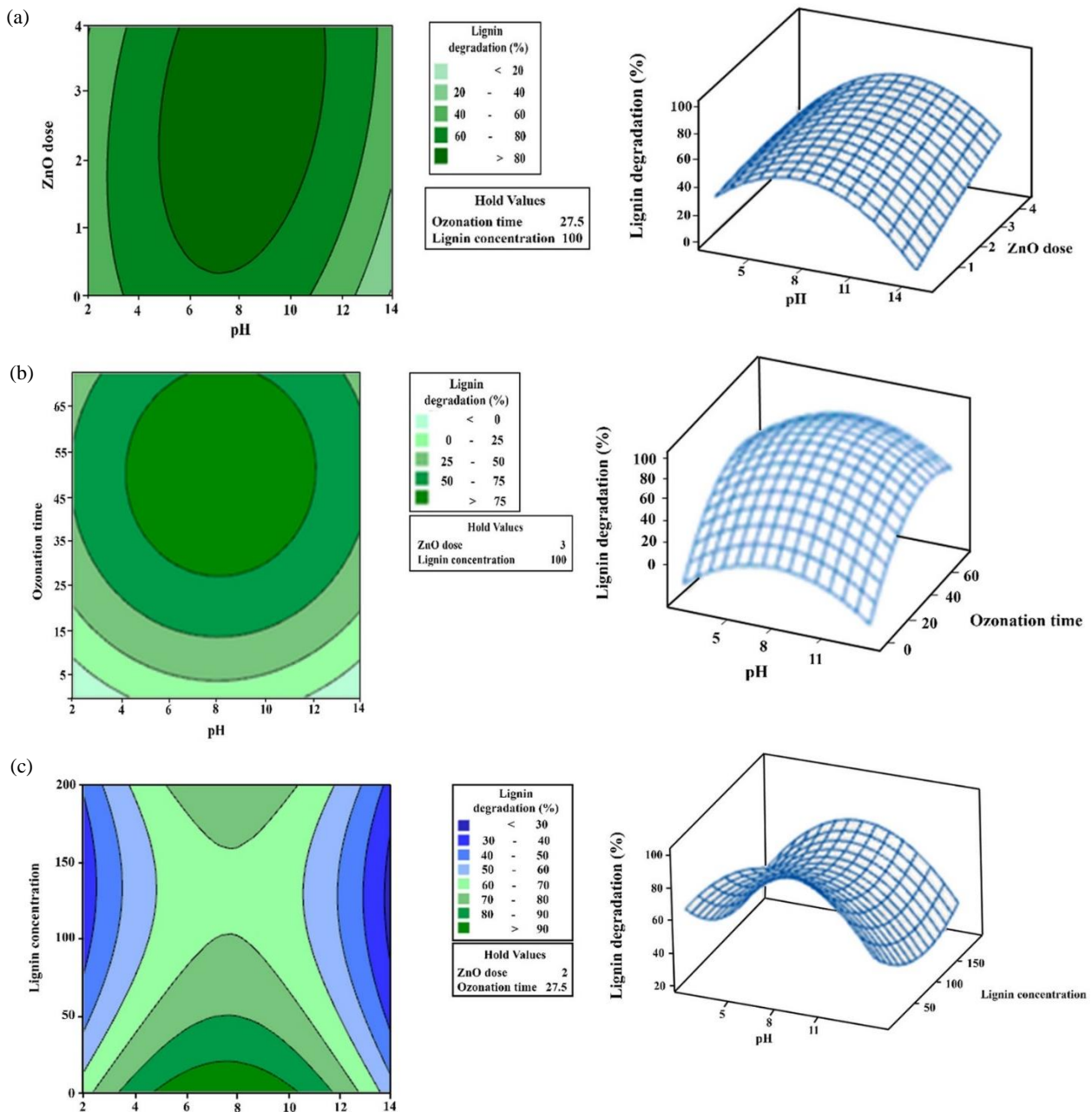
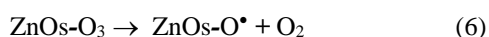


Figure 4. The effectiveness of pH solution on lignin degradation by ZnO COP, (a) ZnO dosage (g/L), (b) ozonation time (min) and (c) lignin concentration (mg/L)

The pH solution influences the form in which lignin molecules exist, the decomposition of ozone and interactions with hydroxyl group on ZnO catalyst surface. It is well established that ozone resonance reacts preferentially with functional group complexes (OCH_3) and $\text{C}=\text{C}$ bond of aromatic in acidic conditions through selective reactions. On the contrary, in alkaline conditions, ozone molecules decompose to produce hydroxyl radicals, superoxide radicals, and hydrogen superoxide radicals, which are substances whose oxidizing power reacts non-selectively with organic substances, thus, together with the catalyst, promoting the formation of more

hydroxyl radicals, which are beneficial for the decomposition of conjugated double bonds, functional groups of organic substances with complex lignin structures (Amini et al., 2023; Norabadi et al., 2020). Increasing the pH accelerates the rate of ozone decomposition through ZnO catalytic reactions. Due to the formation of highly reactive radicals (such as $\text{HO}\cdot$ and others like $\text{OH}\cdot$, $\text{HO}_2\cdot$, and $\text{HO}_3\cdot$), enhances the degradation rate of lignin. Based on Figures 4(a)-(c), it was found that the optimal pH for lignin degradation of ZnO catalytic ozonation process is 8. Moreover, the catalytic potential of ZnO in the ozonation process for lignin degradation confirmed.

The results of this study are consistent with Zhao et al. (2009) who used zinc catalyst to degrade nitrobenzene with an increase in pH value of 11. Phenols are one of the most important constituents in the structure of lignin that it removed by catalytic ozonation in pH solution of the neutral to weak alkaline range (pH 7-8). As stated by Li et al. (2018), in alkaline conditions, the metal oxide catalyst can capture ozone molecules and be in the state of a particle that breaks down to 1 oxygen molecule. Then, it will react with water to form metal oxides and hydroxyl radicals that can oxidize the double bonds or functional groups of the pollutants to be removed, promoting the formation of hydroxyl radicals and ZnO-hydroxyl radicals (oxidation radicals), thus increase the efficiency of the degradation of pollutants. The following mechanisms have been proposed for the formation of these hydroxyl and ZnO-hydroxyl radicals in Equation 5-7).



3.3.2 Effective of ZnO dosage

As shown in Figure 5(a), an increase in lignin degradation is observed with higher amounts of ZnO nanoparticles and longer ozonation times. At 100 mg/L lignin concentration and pH 8, when the operating time exceeded 40 min and the ZnO dosage exceeded 2 g, lignin degradation efficiency exceeded 80%. Figure 5(b) demonstrates the combined effect of ZnO dosage to lignin on the rate of lignin degradation. Under constant conditions, initial pH (8) and operating

time of 27.5 min, an increase in lignin concentration can reduce degradation rate. Specifically, at lignin concentrations greater than 100 mg/L, the efficiency of the process decreased despite the increase in ZnO nanoparticles.

The lignin degradation ability by ZnO was low when the ozone exposure time was short. When the amount of ZnO was more than 2 g and the ozonation time increased to 30 min, the degradation efficiency was 80%. It shows that when the number of catalysts is higher, the surface area of the metal oxide catalyst is larger, the surface hydroxyl groups are increasingly reactive with ozone, resulting in the elimination of functional groups or conjugate bonds in the lignin structure, and lower color value for the decomposition of ozone molecules and the subsequent reactions. Like observed in previous studies, including those by Shao et al. (2009) on catalytic ozonation of nitrobenzene (with ZnO) removal through metal oxide catalytic ozonation. Additionally, as noted by Rosal et al. (2008), increasing catalyst concentration at a fixed ozone flow rate can enhance the transfer of ozone from the gas phase to the aqueous phase, thereby accelerating ozone molecule decomposition.

3.3.3 Ozonation time effective

The effectiveness of ozonation time (minutes) and lignin concentration (mg/L), while two variables (pH=8 and ZnO dose=2.0 g) were constant. As shown, the lignin removal increased with an extended ozonation operating time. ZnO catalytic efficiency increased from 69.30% to 99.6% as the ozonation time was increasing from 20 to 50 minutes. However, higher lignin concentration negatively affected lignin degradation shown in Figure 6.

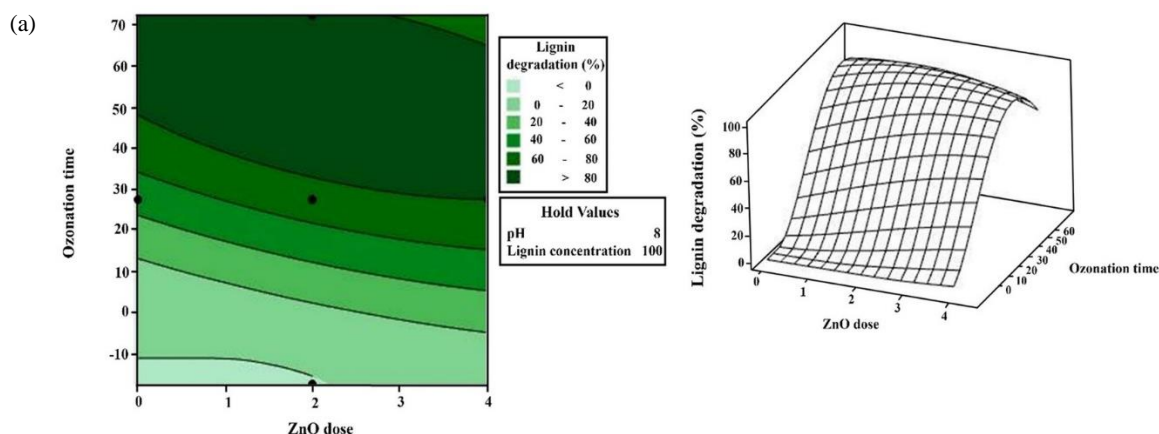


Figure 5. The effectiveness of ZnO dosage on lignin degradation by ZnO catalytic ozonation process, (a) ozonation time (min) and (b) initial lignin concentration (mg/L)

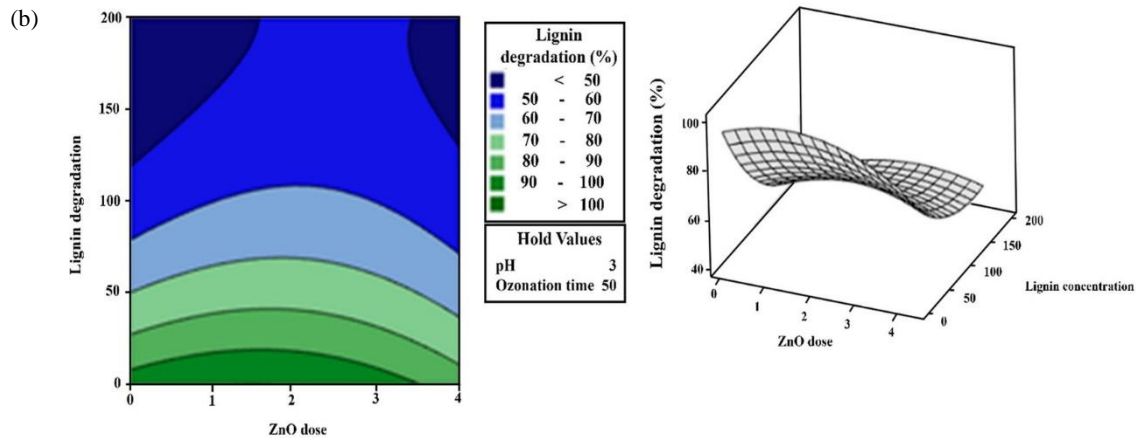


Figure 5. The effectiveness of ZnO dosage on lignin degradation by ZnO catalytic ozonation process, (a) ozonation time (min) and (b) initial lignin concentration (mg/L) (cont.)

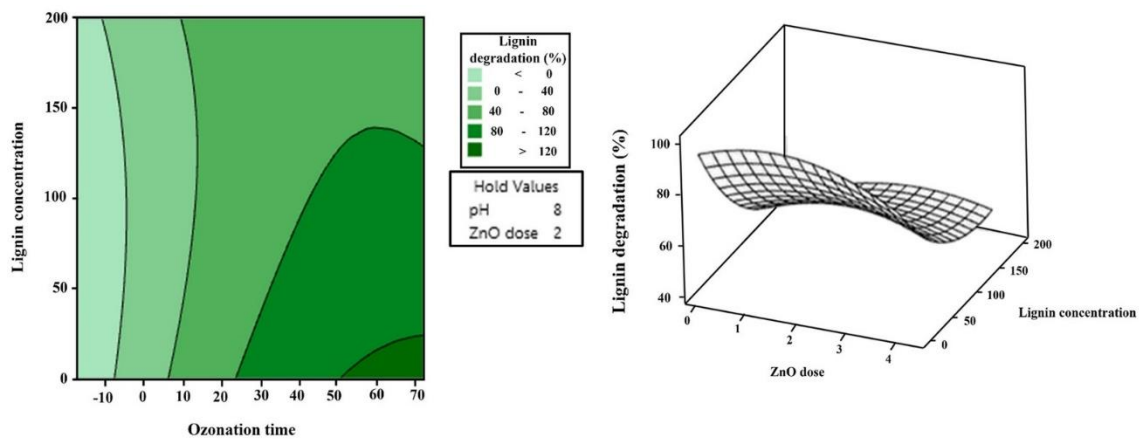


Figure 6. The effectiveness of ZnO catalytic ozonation with varying catalyst dosage by RSM

The effect of ozonation operating time is a crucial factor in achieving the desired purification objectives, as it plays a crucial role in the design and operation of the oxidation process. Ozonation operating time increased and lignin concentration decreased. Similar observations which were studied by Yaghmaeian et al. (2014) on amoxicillin antibiotic degradation and mineralization through catalytic ozonation (NH_4Cl). The catalytic activity of ZnO in lignin degradation attributed to hydroxyl group on surface which attract ozone ion to produce hydroxyl

radical high oxidizing agent for the decomposition sulfonated soda lignin due to color reduction.

3.3.4 Equation fitting model test

Two runs of additional experiments evaluated to confirm the equation fitting model. Table 5 depicts lignin degradation efficiency as a function of the chosen conditions for ZnO dosage, the initial pH, the initial lignin concentration, and ozonation time. These two trials gave results close to the estimation, proving fitting model reliability. Figure 7 showed the lignin solution in each experiment.

Table 5. Confirmation experiments

Conditions	A	B (g/L)	C (mg/L)	D (min)	Lignin degradation (%)	
					Experimental	Predicted
1	8	2	50	60	80.53	81.1
2	8	3	50	60	89.92	79.23

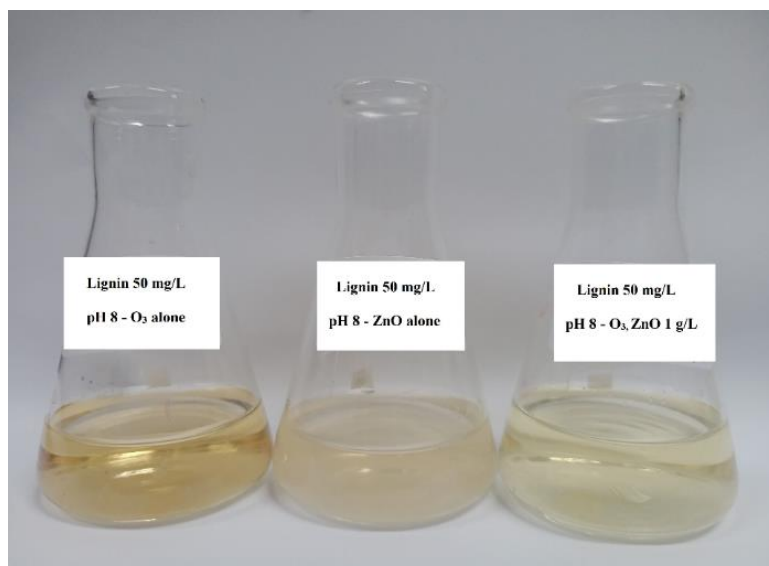


Figure 7. Lignin treatment by Catalytic ozonation ZnO nanoparticles on operating time 50 mins

4. CONCLUSION

In conclusion, the effectiveness of ZnO catalytic ozonation for lignin degradation in synthetic wastewater was investigated. A CCD combined and RSM was applied to model the relationships between key factors, including pH, ZnO dosage, ozonation time, and initial lignin concentration, to determine the optimal operational conditions. The experimental data revealed that lignin degradation increased with higher pH, ZnO dosage, and ozonation operating time. However, increased lignin concentration negatively impacted process efficiency. The predicted results suggested that optimal lignin degraded (99.6%) in pH 8, ZnO dose 1.0 g/L, ozonation operating time 50 minutes, and an initial lignin concentration 50 mg/L. Under these conditions, the experimental degradation rate reached 89.99%. Overall, the study concluded that ZnO nanoparticles are an effective catalyst for lignin degradation and mineralization in the catalytic ozonation process.

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AUTHOR CONTRIBUTIONS

Conceptualization, Aiyathiti C; Methodology, Aiyathiti C, Amnath Y; Validation, Aiyathiti C, Amnath Y; Formal Analysis, Amnath Y; Investigation, Aiyathiti C, Amnath Y; Resources, Aiyathiti C; Data Curation, Amnath

Y; Writing-Original Draft Preparation, Amnath Y; Writing-Review and Editing, Aiyathiti C; Visualization, Amnath Y; Supervision, Aiyathiti C; Project Administration, Aiyathiti C; Funding Acquisition, Aiyathiti C.

DECLARATION OF CONFLICT OF INTEREST

The authors declare no conflict of interest.

REFERENCES

- Amini M, Hosseini S, Chaibakhsh N. High-performance NiO@Fe₃O₄ magnetic core-shell nanocomposite for catalytic ozonation degradation of pharmaceutical pollution. *Environmental Science and Pollution Research* 2023; 30(43):98063-75.
- Einaga H, Sano Y, Minakata D, Yamaguchi A. Fundamental insights and recent advances in catalytic ozonation. *Applied Catalysis B: Environmental* 2024;350:Article No. 123591.
- Hanapi NHM, Abdullah SHYS, Ismail AB, Juahir H. Central composite design: A response surface methodology approach in biodegradation of textile dye wastewater. *Journal Korean Society Environmental Engineering* 2021;43(6):461-75.
- Haqa I, Mazumder P, Kalamdhad AS. Recent advances in removal of lignin from paper industry wastewater and its industrial applications: A review. *Bioresource Technology* 2020;312:Article No. 12363.
- Hayat K, Gondal MA, Khaled MM, Ahmed S, Shamsi AM. Nano ZnO synthesis by modified sol gel method and its application in heterogeneous photocatalytic removal of phenol from water. *Applied Catalysis A: General* 2011;393(1-2):122-9.
- Li J, Zhang M, Li J, Wang D. Corn stover pretreatment by metal oxides for improving lignin removal and reducing sugar degradation and water usage. *Bioresource Technology* 2018;263:232-41.
- Li X, Liu J, Zhang Y, Chen G. Application of heterogeneous catalytic ozonation in wastewater treatment: An overview. *Catalysts* 2023;13(2):Article No. 342.
- Kumar A, Srivastava NK, Gera P. Removal of color from pulp and paper mill wastewater-methods and techniques: A review.

- Journal of Environmental Management 2021;298:Article No. 113527.
- Mao H, Li J, Wang X, Zhang T. Co-Mn bimetallic oxide catalyzed continuously ozonation of lignin into aromatic aldehydes. Industrial Crops and Products 2025;220:Article No. 117615.
- Mohammadi L, Bazrafshan E, Noroozifar M, Moghaddam AA. Application of heterogeneous catalytic ozonation process with magnesium oxide nanoparticles for toluene degradation in aqueous environments. Health Scope 2016;5(4):e40439.
- Nawrocki J, Kasprzyk-Hordern B. The efficiency and mechanisms of catalytic ozonation. Applied Catalysis B: Environmental 2010;99(1-2):27-42.
- Norabadi E, Panahi AH, Reza Ghanbari R, Meshkinian A, Kamani H, Ashrafi SD. Optimizing the parameters of amoxicillin removal in a photocatalysis ozonation process using Box-Behnken response surface methodology. Desalination and Water Treatment 2020;192:234-40.
- Rosal R, Rodríguez A, Perdigón-Melón JA, Mezcua M, Hernando MD, Letón P, et al. Removal of pharmaceuticals and kinetics of mineralization by O_3/H_2O_2 in a biotreated municipal wastewater. Water Research 2008;42(14):3719-28.
- Zhao L, Sun Z, Ma J. Novel Relationship between hydroxyl radical initiation and surface group of ceramic honeycomb supported metals for the catalytic ozonation of nitrobenzene in aqueous solution. Environmental Science and Technology 2009; 43(11):1-11.
- Zhao R, Zong S, Ma QQ, Xu Z, Yuan J. Investigating the electrocatalytic properties of ZnO-based composite membrane for dye removal. Scientific Reports 2025;15:Article No. 6306.
- Zhou C, Liu S, Wang Q. Catalytic ozonation for pulp and paper mill wastewater treatment: COD reduction and organic matter degradation mechanism. Separations 2023;10(3):Article No. 148.
- Yaghmaeian K, Moussavi G, Alahabadi M. Removal of amoxicillin from contaminated water using NH_4Cl -activated carbon: Continuous flow fixed-bed adsorption and catalytic ozonation regeneration. Chemical Engineering Journal 2014;236:538-44.