



Research article

Lignin removal from synthetic wastewater via Fenton-like reaction over Cu supported on MCM-41 derived from bagasse: Optimization and reaction intermediates

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ABSTRACT

Lignin degradation was performed using a Fenton-like oxidation reaction with Cu supported on MCM-41, derived from bagasse (Cu-BG-MCM-41), as the catalyst. The optimal degradation conditions required to remove a predetermined amount of lignin (95%) from an effluent were determined. Based on the literature review and preliminary tests, the critical parameters determining the operating conditions include temperature, catalyst loading, pH, H₂O₂ concentration, and reaction time. The experimental design and working conditions were based on Box–Behnken design. The reaction products were analyzed via UV–vis and gas chromatography–mass spectrometry. Response surface methodology (RSM) was used to predict the optimum operating conditions for the Fenton-like reaction for 95% lignin degradation, which were a temperature of 80 °C, initial pH of 9, H₂O₂ concentration of 1 mL/L, catalyst loading of 1.0 g/L, and reaction time of 30 min. These conditions were validated three times and the achieved percentage of lignin degradation was 95 ± 2%. This is close to the value of 95% used in the RSM to determine the optimum operating conditions, thus verifying the model. The catalyst was stable and functioned well under the optimum design conditions. Moreover, the reaction could be used to obtain high-value intermediate products if stopped after 5 min. Finally, lignin was degraded into vanillin, a higher-value product. As expected, the proposed Fenton-like approach expanded the pH working range from less than 4 to 5–9.

1. Introduction

The production of pulp and paper requires the consumption of very large amounts of water and other resources, and significant quantities of effluent are inevitably generated. The presence of lignin in the wastewater resulting from pulp and paper manufacturing contributes to an alarmingly high level of pollutants that have high chemical oxygen demand (COD), a significant biochemical oxygen

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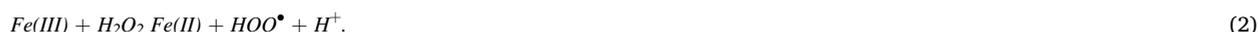
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demand (BOD), and are rich in dissolved solids. The chemical makeup of this wastewater has a negative environmental impact, and dark coloration adversely affects aquatic life. Lignin and its derivatives are the major contributors responsible for the toxicity and color of the effluent generated during the manufacture of pulp and paper.

Lignin is the general term used to refer to a large group of aromatic compounds and impervious polymers resulting from the oxidative coupling of 4-hydroxyphenylpropanoids. These compounds are predominantly present in woody plants, and they are difficult to degrade. Untreated wastewater from pulp and paper mills is typically directly discharged into aquatic environments. This effluent contains significant quantities of solid content and a high organic load, which affects aquatic ecosystems in various ways. For instance, exposure to pulp and paper effluent can affect fish reproduction and physiology, lead to localized benthic community damage, and cause oxygen depletion in large areas [1,2].

Biological treatments are now the preferred strategy for removing lignin from pulp and paper wastewater [3–5]. However, eliminating lignin, which is a large group of polymers, from pulp and paper effluent via biological treatment is challenging. Adsorption is an efficient and economical strategy for treating wastewater; however, removing waste from effluent is difficult [6,7]. Advanced oxidation processes (AOPs) continue to be considered the best methods for lignin degradation. Sriprom et al. [8–11] used wet air oxidation to achieve a higher reaction efficiency. However, this process required high pressure and temperature. Fenton reactions are AOPs that operate at standard pressure and temperature and can be used to degrade pollutants at a lower cost, such as the degradation of Penicillin G (FEN G) [12]. As indicated in Eqs. (1) and (2), the Fenton reaction is an aqueous reaction between an iron-based catalyst and hydrogen peroxide that generates strongly reactive hydroxyl radicals (OH^\bullet). The oxidation of organic contaminants or wastewater can be achieved in Fenton-based processes. Ferric and ferrous ions react with peroxide as follows:



The Fenton reaction requires the pH to be regulated in the acidic range of 3–4. This, along with the requisite production of iron sludge resulting from the coagulation of ferrous and ferric ions in the final process, is a significant disadvantage of Fenton processes. The use of additional acid to adjust the pH of waste within the defined parameters incurs an additional cost. In this study, the Fenton reaction is modified using copper ions as the catalyst, which operates at pH = 5–7. Copper is coated on MCM-41 derived from bagasse (BG-MCM-41), as described in our previous work [13]. 5 wt% Cu-BG-MCM41 and 10 wt% Cu-BG-MCM41 catalysts prepared by an in-situ hydrothermal method have BET specific surface areas of 725 and 357 m^2/g , respectively, which are higher than those of 5 wt% Cu-BG-MCM41 (621 m^2/g) and 10 wt% Cu-BG-MCM41 (332 m^2/g) prepared via impregnation method. The modified process, referred to as a Fenton-like reaction, is used in this work to evaluate the optimum reaction conditions for lignin removal from wastewater.

The objectives of this study are to assess lignin degradation through a Fenton-like reaction using Cu-BG-MCM-41 as a catalyst to optimize the reaction parameters (temperature, pH, amount of catalyst, H_2O_2 concentration, and time) using response surface methodology (RSM) and to explore the high-value intermediate products and by-products.

2. Experimental

2.1. Chemicals

Lignin was obtained from Sigma Aldrich (Germany) to prepare synthetic pulp and paper wastewater. The lignin solution (350 mg/L) was prepared by using distilled water to dissolve 0.35 g of lignin and adjusting the pH to 10 with 1 M sodium hydroxide (NaOH) and nitric acid (5% HNO_3) (Analytical grade, Ajax Finechem, Australia). Hydrogen peroxide (30% w/w) was obtained from QREC (New Zealand). 5% Cu-BG-MCM-41 was synthesized via hydrothermal method for use as a Fenton-like reaction catalyst. The chemicals used for catalyst synthesis were obtained from UNILAB (Thailand) and LAB SCAN (Thailand). The characterization of the 5% Cu-BG-MCM-41 catalyst was reported in our previous work [13].

2.2. Optimization experimental design

Box–Behnken design (BBD) and RSM were used to optimize the experimental conditions for using 5% Cu-BG-MCM-41 as a catalyst to degrade lignin in a Fenton-like reaction. BBD and RSM are typically used for experimental design, model building, and investigating the effects of different variables. BBD can be used to arrange up to five factors in orthogonal blocks. This technique showed that a second-order model could be expanded to include block effects without affecting the estimation of optimal parameters; the effects are

Table 1

Experimental design for using 5% Cu-BG-MCM-41 catalyst to degrade lignin in Fenton-like reaction.

Independent variable	Code	Level minimum (–1)	Level medium (0)	Level maximum (+1)
Temperature ($^\circ\text{C}$)	X_1	60	70	80
pH	X_2	3	6	9
Catalyst loading (g/L)	X_3	0	0.5	1
H_2O_2 (mL/L)	X_4	0	0.5	1
Reaction time (min)	X_5	5	15	30

orthogonal to the block effects. Orthogonal blocking is beneficial when experiments are arranged in blocks and the block effects are likely to be significant. Thus, this approach allows the evaluation of the factors influencing lignin degradation in addition to the interactions between these factors. MINITAB software (version 16.0) was used for experimental design, analyzing data, building the quadratic model, and plotting graphs. The independent variables (reaction temperature, initial pH, catalyst loading, H₂O₂ concentration, and reaction time) were coded as low level (−1) and high level (+1) in the BBD, as indicated in Table 1. The software generated 46 experiments under the experimental conditions listed in Table 2. The lignin degradation percentage (Y%) was the measured response, which was calculated using Eq. (3) as follows:

$$Y (\%) = ((C_0 - C_i) / C_0) \times 100\%, \quad (3)$$

where C₀ is the initial lignin concentration and C_i is the lignin concentration after 30 min of reaction (mg/L).

2.3. Experimental protocol

Fenton-like oxidation experiments were performed in 500 mL flasks with magnetic stirrers. To perform each experiment, 300 mL of the lignin solution was transferred to a flask. As required, the initial pH was modified with NaOH and HCl. Specific amounts of 5% Cu-BG-MCM-41 and H₂O₂ (30% v/v) were added. The experiments were conducted based on the experimental conditions listed in Table 2,

Table 2
Box–Behnken design of lignin degradation via Fenton-like reaction.

Run order	Temperature (°C)	pH	Catalyst load (g/L)	H ₂ O ₂ (mL/L)	Reaction time (min)	Experimental lignin degradation (%)	Predicted lignin degradation (%)
1	70	3	1.0	0.5	15	23.07	47.06
2	70	9	0.0	0.5	15	33.33	34.40
3	70	6	1.0	0.5	30	105.03	97.48
4	60	6	0.5	0.0	15	51.46	50.70
5	60	6	0.0	0.5	15	48.16	47.77
6	70	6	0.0	0.5	5	45.70	50.40
7	60	3	0.5	0.5	15	44.23	52.02
8	70	6	0.5	0.5	15	34.06	50.09
9	70	3	0.5	0.0	15	29.85	34.55
10	70	3	0.5	0.5	30	106.32	78.47
11	70	6	1.0	1.0	15	91.57	87.41
12	60	6	0.5	0.5	5	53.66	55.06
13	80	6	0.5	1.0	15	71.15	76.31
14	80	6	0.5	0.5	5	38.19	37.79
15	60	6	0.5	0.5	30	48.81	60.11
16	70	6	1.0	0.5	5	45.51	44.72
17	70	6	0.5	0.5	15	56.87	50.09
18	80	6	0.5	0.5	30	74.08	83.58
19	80	9	0.5	0.5	15	72.62	64.12
20	70	6	0.5	0.5	15	59.34	50.09
21	70	6	0.5	0.0	30	35.27	38.30
22	70	9	0.5	0.5	5	52.02	62.05
23	70	6	0.5	1.0	30	96.34	102.11
24	60	6	1.0	0.5	15	76.47	64.48
25	70	6	0.5	0.5	15	44.59	50.09
26	70	6	0.5	0.0	5	50.18	54.18
27	70	6	0.0	0.5	30	50.55	48.49
28	70	6	0.5	1.0	5	28.66	35.38
29	80	6	0.0	0.5	15	48.54	45.93
30	80	3	0.5	0.5	15	41.58	51.00
31	70	6	0.5	0.5	15	48.54	50.09
32	60	6	0.5	1.0	15	53.21	55.99
33	70	9	0.5	0.5	30	56.32	64.17
34	70	6	0.0	1.0	15	52.11	47.17
35	70	3	0.5	0.5	5	55.40	29.75
36	70	3	0.5	1.0	15	65.29	65.20
37	80	6	1.0	0.5	15	86.72	72.53
38	80	6	0.5	0.0	15	34.98	36.59
39	60	9	0.5	0.5	15	67.03	56.90
40	70	6	1.0	0.0	15	48.99	46.32
41	70	9	0.5	1.0	15	77.28	66.05
42	70	6	0.0	0.0	15	46.70	43.25
43	70	3	0.0	0.5	15	50.55	58.24
44	70	6	0.5	0.5	15	57.14	50.09
45	70	9	0.5	0.0	15	58.15	51.69
46	70	9	1.0	0.5	15	71.52	88.89

and samples were taken for analysis. During these experiments, the beakers were fully covered to ensure darkness.

UV-vis spectrophotometry at 280 nm was used to measure lignin degradation. Gas chromatography-mass spectrometry (GC-MS) was performed to analyze intermediate organic species. GC-MS analysis was performed with an Agilent 6890 N gas chromatograph operated in splitless mode coupled with an Agilent 5973 N mass spectrometer operated in electron impact and scan system modes. The injection port temperature was set to 250 °C. The carrier gas was helium (1 mL min⁻¹ flow rate). The column used in the GC instrument was a capillary HP-5 MS (30 m × 0.25 mm × 0.25 μm). The heating program was as follows: holding at 45 °C for 1 min, increasing the temperature to 310 °C at a constant rate of 10 °C·min⁻¹, and maintaining this temperature for 7 min. Quality assurance, control protocols, and analytical instrument performance were determined according to Kaewlaoyong et al. [14,15]. The midpoint standard was recovered within 100 ± 20%, and each unknown peak was identified with the compound database and Library Search Compound (LSC) report. Compounds with qualitative percentages greater than 75% were described.

3. Results and discussion

3.1. RSM for degradation optimization

The BBD with five factors at three levels and the lignin degradation results are displayed in Table 2. A polynomial equation (Eq. (4)) was developed to describe an approximate regression model of the lignin degradation performance:

$$Y = 50.09 + 1.55X_1 + 4.49X_2 + 10.83X_3 + 11.25X_4 + 12.71X_5 + 3.22X_1^2 + 2.69X_2^2 + 4.36X_3^2 + 1.58X_4^2 + 5.82X_5^2 + 2.06X_1X_2 + 2.47X_1X_3 + 8.61X_1X_4 + 10.19X_1X_5 + 16.42X_2X_3 - 4.08X_2X_4 - 11.65X_2X_5 + 9.29X_3X_4 + 13.67X_3X_5 + 20.65X_4X_5, \quad (4)$$

In Eq. (4), Y is the efficiency of lignin degradation; X₁ is the coded variable of temperature (°C), X₂ is the initial pH, X₃ is the catalyst loading (g/L), X₄ is the H₂O₂ concentration (mL/L), and X₅ is the reaction time (min).

One of the objectives of this experimental design was developing a reliable and simple model capable of directly relating the response to the most significant variables. A factor was considered to be significant in Eq. (4) if its P-value (the probability that noise was responsible for the correlation between a factor and the response) was below 0.05. Backward elimination was used to remove insignificant factors, and the significant factors were retained to model the data [16]. However, despite the insignificance of the pH factor (P > 0.05), pH is included in the mathematical model due to its interaction with catalyst loading. Subsequently, the experimental response of the lignin degradation was reduced as follows:

$$Y = 79.60 - 3.97X_2 - 71.33X_3 - 18.79X_4 - 1.44X_5 + 10.94X_2X_3 + 1.82X_3X_5 + 2.75X_4X_5, \quad (5)$$

The coefficient of determination R², which was 0.6137, was used to verify the accuracy of the model. This indicated that the model was able to describe 61.37% of the response variation. Analysis of variance (ANOVA) was performed by using an F-test to evaluate the statistical significance of the model equation (Table 3). The ANOVA evaluation provided insight into the significance of the relationship between the system parameters and the system response as well as the variance of the results [17,18]. The model had an F-value of 2.13, which implied that the model was significant, with a low 0.01% chance that this F-was caused by noise. The extremely low P-value (P < 0.05) demonstrated the significance of this model. "Prob > F" values below 0.05 indicated the significance of the model terms. The lack-of-fit test was used to evaluate the adequacy of the fitted model, and the lack-of-fit P-value was 0.078. Residual error is a statistic that consists of lack-of-fit error and pure error. The significance of the lack-of-fit error is measured by the lack-of-fit P-value. The variation in response for each set of conditions is described by the pure error. For a set of replicates, the pure error is defined as the sum of the squared deviations of the responses from the mean response. In contrast, the error caused by a model deficiency is described by the lack-of-fit error. If the data is well-fitted by the model, the pure error and mean square of the lack-of-fit error will have very similar values. In this case, the resulting F-statistic ratio is small (close to 1). Suppose the P-value of this small

Table 3
ANOVA of regression model for Fenton-like lignin degradation.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	7	10342	10342	1477.42	8.62	0.000
Linear	4	6811.2	6811.2	1702.81	9.94	0.000
pH	1	323.8	323.8	323.8	1.89	0.177
Catalyst loading	1	1876.2	1876.2	1876.2	10.95	0.002
H ₂ O ₂	1	2025.8	2025.8	2025.8	11.82	0.001
Reaction time	1	2585.4	2585.4	2585.4	15.09	0.000
Interaction	3	3530.7	3530.7	1176.91	6.87	0.001
pH * catalyst loading	1	1077.8	1077.8	1077.91	6.29	0.017
Catalyst loading * reaction time	1	747.2	747.2	747.21	4.36	0.044
H ₂ O ₂ * reaction time	1	1705.7	1705.7	1705.72	9.96	0.003
Residual error	38	6510.6	6510.6	171.33		
Lack-of-fit	25	5232.1	5232.1	209.28	2.13	0.078
Pure error	13	1278.5	1278.5	98.35		
Total	45	16852.6				

F-statistic ratio is higher than the significance level. In this case, the lack-of-fit is insignificant, and the model can be used to satisfactorily describe data within the experimentation region. Conversely, suppose the lack-of-fit error F-statistic is significant (indicating that most of the residual error is caused by lack-of-fit) and the corresponding P-value is small. In this case, the lack-of-fit test is significant. This indicates that the regression model cannot adequately explain variation in the data.

An essential part of analysis is evaluating the adequacy of a proposed model is an essential part of an analysis. Functional adequacy ensures that a real system is adequately approximated by a model. However, it can also yield misleading or poor results [19–21]. Figs. 1 and 2 show diagnostic plots, which were used to estimate if the regression model's fit was adequate. Both the predicted and actual lignin degradation plots are displayed in Fig. 1. The measured values for each run are displayed as the actual lignin degradation, and the model was used to obtain predicted values. The response obtained using the mathematical model's independent variables has a certain amount of variability, which is described by the R^2 value. However, a significant R^2 value does not always imply an acceptable regression model. R^2_{adj} , whose value does not necessarily increase when variables are added, was chosen to determine the regression model fit. As indicated in Fig. 2, an acceptable fit was obtained between the experimental and predicted lignin degradation values. The R^2 value was 0.1637, and the R^2_{adj} value was 0.5425. Therefore, the low R^2 values of the predicted lignin degradation and experimental values plots illustrate that a significant trend can be identified even for relatively noisy data with high variability. The trend indicates that even though the data points are not always close to the regression line, the predictor variable can still provide useful information regarding the response. Thus, the actual values were adequately approximated by the proposed model.

As indicated in Fig. 2, residual plots were used to test if the model satisfied the ANOVA assumption, and four analyses were used to validate the response model. Fig. 2a shows a standard probability plot, which indicates that the experimental data were linearly distributed on a straight line. Thus, the assumption of normality was satisfied. The residual vs. fit plots were randomly scattered, as shown in Fig. 2b. Across the predicted value range, the data exhibited a relatively constant variance. An overturned bell shape was observed in the histogram chart, as shown in Fig. 2c. This implies that no apparent problems were present in the standard curve. A residual vs. order plot is displayed in Fig. 2d. This plot shows the existence of random scatter fluctuations around the centerline (± 2 range). Therefore, the experimental data were well-distributed and the data of the fitted model had acceptable accuracy and reliability [22].

3.2. Factors influencing Fenton-like reaction for lignin degradation

Heating (to 60, 70, and 80 °C) had a positive influence on lignin degradation, as displayed in Fig. 3a. However, the result was insignificant. The lignin degradation efficiency rose from 55% to 60% when the reaction temperature rose from 60 to 80 °C. Raising the reaction temperature increases the number of collisions between reacting molecules, leading to a higher reaction rate. The Fenton-like reaction rate can therefore be enhanced by increasing the reaction temperature to accelerate hydroxyl radical generation [23]. These results demonstrate that a Fenton-like reaction can operate in mild conditions, and when compared with other wet oxidation methods used in severe conditions, lignin was completely degraded to carbon dioxide, water, and small carboxylic acids [8].

Other reported lignin degradation treatments have indicated that temperature does significantly influence lignin degradation, as listed in Table 4. Increasing the reaction temperature leads to the formation of more hydroxyl radicals, which enhances the rate of lignin degradation and the rates of side reactions. At lower reaction temperatures of approximately 20–40 °C, it is commonly reported that the remediation efficiency can be improved by increasing the reaction temperature. This is because higher temperatures provide more energy, so the reaction's activation energy can be overcome and a higher reaction rate constant can be obtained, as indicated by the Arrhenius equation. However, these degradation processes used temperatures much lower than the 60–80 °C temperature range studied in this work. A high reaction temperature of 145 °C was utilized for catalytic wet peroxide oxidation (CWPO) lignin degradation [27] (using vanillic as a model lignin) with 30 wt% hydrogen peroxide. However, only 78% lignin degradation was reported, lower than that achieved in this work. This and other processes are compared in Table 4.

Solution pH also influences lignin degradation in the Fenton-like reaction, as indicated in Fig. 3b. Although the solution pH was

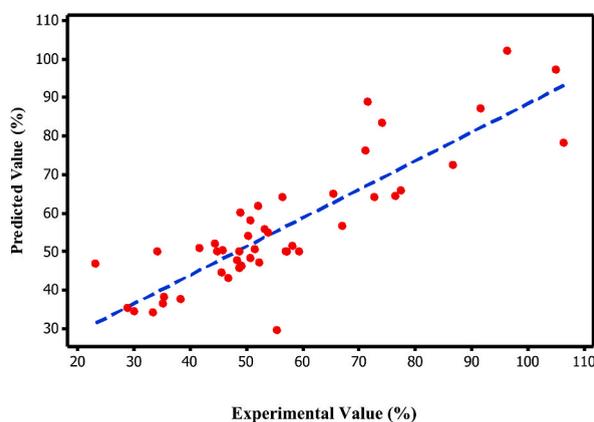


Fig. 1. Predicted values vs. experimental values (%) for the removal of lignin from synthetic wastewater.

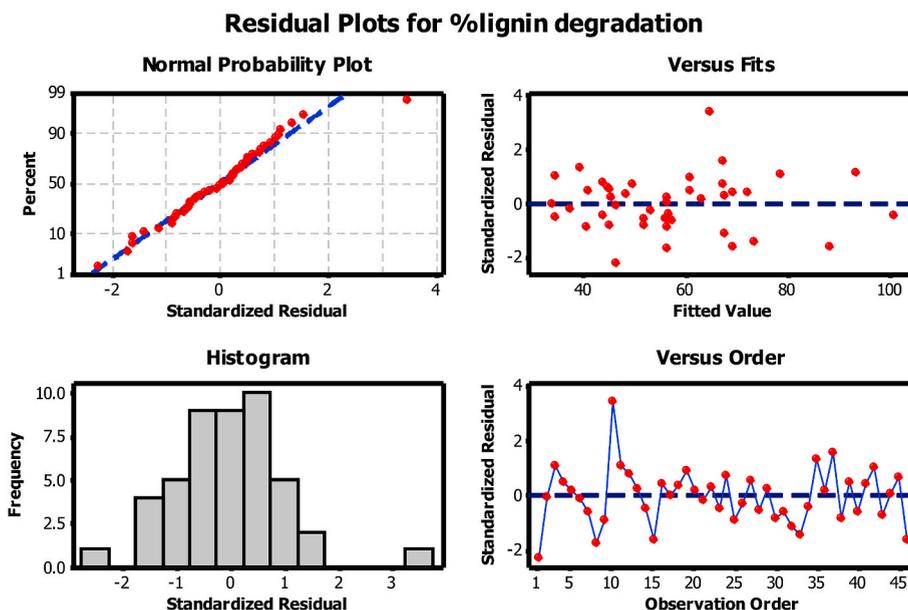


Fig. 2. (a) Normal probability vs. standardized residual, (b) standardized residual vs. fitted values, (c) standardized residual histogram, and (d) standardized residual vs. observation order.

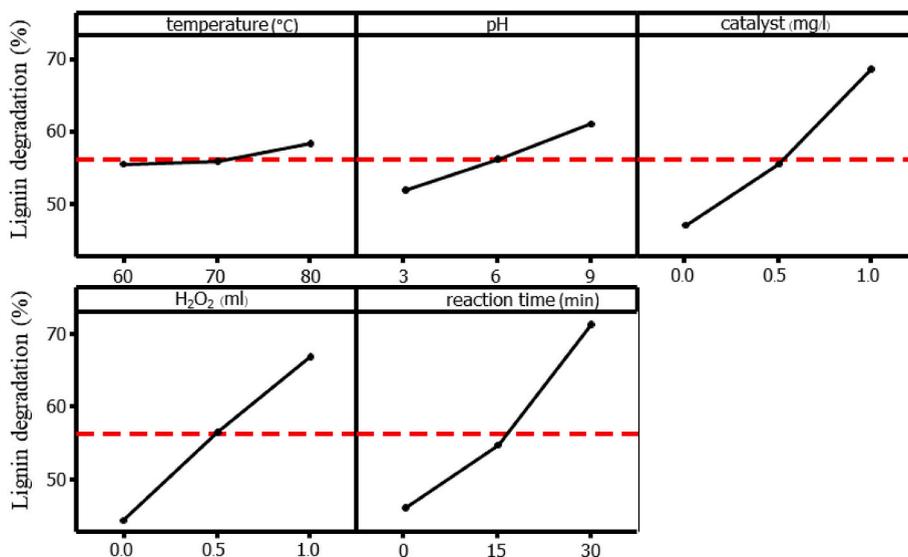


Fig. 3. Plots of the effects of Fenton-like reaction parameters on lignin degradation.

insignificant in ANOVA analysis, the other parameters were affected by the pH. Lignin oxidation was directly affected by the solution pH because it affected the variation of Cu^+ ions and the generation rate of hydroxyl radicals, which were responsible for lignin oxidation [28]. The influence of pH on lignin degradation was considered at initial pH values of 3, 6, and 9, and the results indicated a marked effect of pH on lignin degradation (Fig. 3b). When the pH was increased from 3 to 9, lignin degradation increased from 50% to 65%. Therefore, this confirms that copper can extend the pH range to facilitate oxidation in an alkaline solution. In this work, the highest degradation was obtained using a Fenton-like reaction at a pH of 9.0.

The influence of catalyst loading on lignin degradation is displayed in Fig. 3c. Increasing the Cu^+ concentration enhanced lignin degradation from 45 to 70%. Fu, Wang, and Tang [18] reported that additional $\cdot\text{OH}$ radicals can be generated by the reaction of Cu^+ ions with hydrogen peroxide, which can degrade organic pollutants into smaller molecules [29]. Other researchers have found that $\cdot\text{OH}$ radicals can recombine when the catalyst concentration increases [30]. This demonstrates that the oxidation of organic pollutants can potentially be marginally hindered at high catalyst concentrations.

The effect of H_2O_2 concentration is shown in Fig. 3d. Lignin degradation was improved from 40% to 70% as the H_2O_2 level

Table 4
Lignin degradation using various processes.

Process	Process parameters	Lignin degradation efficiency	Reference
Fenton reaction	- Lignin: 100 mg/L - Catalyst: Fe ⁰ (7.61 mg/L), Fe ²⁺ (9.89 mg/L), Fe ³⁺ : 14.27 mg/L - H ₂ O ₂ : 376.88 mg/L - pH 3 - Temperature: 35 °C	98.45%	[24]
Fenton-like reaction	- Vanillic (lignin model): 35 mg/L - GO-Fe ₃ S ₄ catalyst load: 0.4 g/L - H ₂ O ₂ : 12 mM - pH 4 - Temperature: 35 °C	94.3%	[25]
Alkaline peroxide	- Extract from rice husk - H ₂ O ₂ : 1% w/v - NaOH: 5.9% w/v - Temperature: 20 °C	59.85%	[26]
Catalytic wet peroxide oxidation (CWPO)	- Vanillic (lignin model): 10 g/L - Titanium silicalite-1 (TS-1) catalyst - H ₂ O ₂ : 30%wt - pH 4 - Temperature: 145 °C - Reaction time: 120 min	78%	[27]
Fenton-like reaction	- Lignin solution: 350 mg/L - Catalyst loading: 1.0 g/L - H ₂ O ₂ : 1 mL/L - pH 9 - Temperature: 80 °C	95%	This work

increased from 0 to 1 mL/L. The amount of available $\bullet\text{OH}$ was assumed to rise as the H₂O₂ concentration was increased. This would enhance oxidation of the organic compounds. However, at concentrations higher than a certain limit, $\bullet\text{OH}$ efficiently reacts with H₂O₂ to produce HO₂ \bullet radicals. These radicals are not very reactive compared with $\bullet\text{OH}$ radicals. Thus, raising the H₂O₂ concentration beyond a certain limit results in a negligible contribution to oxidation [31]. The reaction time (Fig. 3e) was mainly influenced by the $\bullet\text{OH}$ formation rate as well as the reaction rate of $\bullet\text{OH}$ with the organic compounds.

Fig. 4a–c shows two-dimensional contour plots that illustrate the interactive effects of initial pH and catalyst loading (Fig. 4a), H₂O₂ concentration and reaction time (Fig. 4b), and catalyst loading and reaction time (Fig. 4c) on lignin degradation by the heterogeneous Fenton-like reaction on Cu-BG-MCM-41. Fig. 4a demonstrates how the interaction of initial pH and catalyst loading influenced lignin degradation. With an initial system pH of 3, lignin degradation decreased with increasing catalyst loading. Conversely, as shown in Fig. 4a, at a higher initial pH of 9, lignin degradation increased with increasing catalyst loading. Fig. 4b illustrates that at a low H₂O₂ concentration, lignin degradation decreased with reaction time. Conversely, with a high concentration of H₂O₂, lignin degradation increased with reaction time. As shown in Fig. 4c, a higher catalyst loading causes lignin degradation to increase with increasing reaction time. Fig. 4a–c only demonstrate the interactions between each pair of variables. However, in a real system, all variables interact with one another. Therefore, MINITAB was used to predict the optimum conditions for the Fenton-like degradation of lignin.

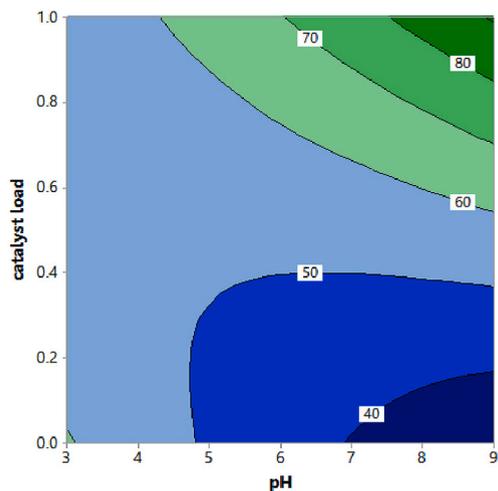
3.3. Optimum conditions and model verification

The performance of the Fenton-like reaction for lignin-degradation efficiency widely varied with changing variables and interactions among the variables. In this study, a target lignin degradation efficiency of 95% was selected because wastewater treated to this quality meets Thailand's regulations. With the lignin degradation efficiency set at the target value, Eq. (5) was used in MINITAB to predict that the optimum Fenton-like reaction conditions were a reaction temperature of 80 °C, an initial pH of 9.0, a catalyst loading of 1.0 g/L, a H₂O₂ concentration of 1 mL/L, and a reaction time of 30 min. Under these predicted optimum conditions, our experiment verified that 95 ± 2% of the lignin could be degraded in three tests. Therefore, the predicted and experimental results were in excellent agreement, demonstrating the suitability of the prediction model for lignin degradation.

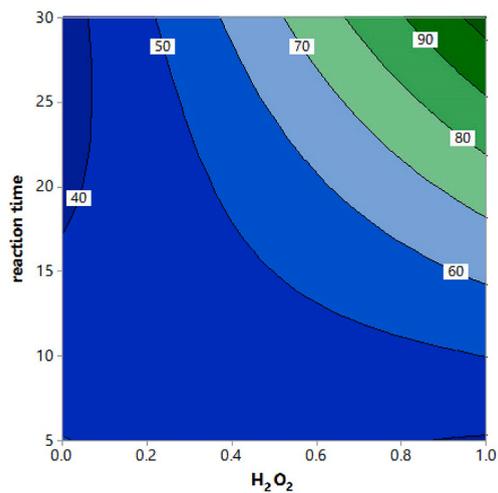
The dissolution of copper in the solution was analyzed by atomic absorption spectroscopy. The treated wastewater contained 1 ppm copper, which was less than 0.01% of the copper loaded on the catalyst. This suggests that this effluent is suitable for discharge into the environment, and the catalyst is stable and functions well under these conditions.

GC-MS was used to identify the intermediate compounds produced during the reaction. The compounds, which are listed in Table 5, included 2-(2-ethoxyethoxy)ethanol, acetophenone, safrole, vanillin, dimethyl phthalate, dibutyl phthalate, diethyl phthalate, di-n-octyl phthalate, bis(2-ethylhexyl) phthalate, squalene, pentanoic acid, alpha-cardinol, hexanedioic acid, octadecane, and tetradecanoic acid. The concentrations of these intermediate compounds decreased as the reaction time increased. After reacting for 30 min, the concentrations of these compounds rapidly declined, indicating that the oxidative hydroxyl reaction was vigorously initiated.

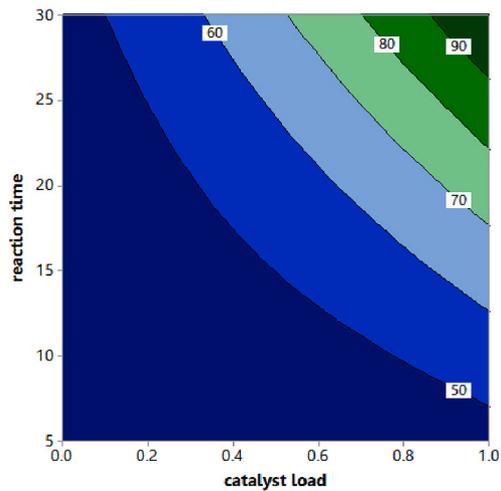
These intermediates indicate that the Fenton-like reaction generated hydroxyl radicals to react with the lignin, which was abundant



(a)



(b)



(c)

(caption on next page)

Fig. 4. Interactive effects of (a) H₂O₂ concentration and reaction time, (b) pH and catalyst loading, and (c) catalyst loading and reaction time.

in the coniferyl alcohol unit. The reaction simultaneously and competitively proceeded via different pathways, including ether and C–C bond hydrolysis and cleavage as well as alkylation, demethoxylation, and condensation. These pathways confirm the findings of Kang et al. [32]. Table 5 indicates that lignin degradation occurred via a mechanism involving three different sequences: (i) lignin was eliminated to alpha-cardinol, vanillin, phthalate derivative compounds, carboxylic acid, CO₂, and H₂O; (ii) lignin was degraded to safrole, phthalate derivative compounds, carboxylic acid, CO₂, and H₂O; and (iii) lignin was cleaved to acetophenone, phthalate-derivative compounds, carboxylic acid, CO₂, and H₂O. Several bacteria and fungus species secrete enzymes that can be utilized for lignin degradation. The intermediates formed by the microbial degradation of lignin include vanillin (4-hydroxy-3-methoxybenzaldehyde), dicarboxylic acid, *cis*-muconic acid, and polyhydroxyalkanoates (PHAs). Therefore, vanillin is a high-value-added intermediate generated from the two approaches [33].

4. Conclusions

Lignin degradation was performed using a Fenton-like reaction, and it was confirmed that the significant operating parameters were the initial pH, catalyst loading, H₂O₂ concentration, and reaction time. The optimal conditions were a reaction temperature of 80 °C, initial pH of 9, catalyst loading of 1.0 g/L, H₂O₂ concentration of 1 mL/L, and reaction time of 30 min. Under optimum conditions, RSM predicted that 95% lignin degradation would be achieved, and three tests under the optimum conditions confirmed lignin degradation of 95 ± 2%. When 95% of lignin in wastewater is degraded, the effluent can be safely discharged into the environment according to Thai wastewater regulations. In addition, the copper leached from the catalyst was found to be less than 0.01% in concentration, meeting legal requirements. Moreover, the Cu-BG-MCM41 catalyst was stable and functioned well under optimum conditions. Based on GC-MS analysis, high-value intermediate products such as vanillin, phthalate-derivative compounds, safrole, and acetophenone could be obtained if the reaction was stopped after 5 min. These products are believed to be generated by partial oxidation reactions. Therefore, using the Cu-BG-MCM41 catalyst in a Fenton-like reaction is suitable for both 95% lignin degradation and obtaining high-value intermediate products.

Author contribution statement

Pongsert Sriprom, Pornsawan Assawasaengrat: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Sutasinee Neramittagapong: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools, or data; Wrote the paper.

Chitsan Lin, Arthit Neramittagapong: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools, or data.

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Table 5
Intermediate compounds formed during Fenton-like reaction under optimal conditions.

Intermediate	Formula	Retention time (min)	Reaction time (min)			
			0	5	10	15
2-(-2-ethoxyethoxy)ethanol	C ₆ H ₁₄ O ₃	10.76	1.91	1.43	ND	1.05
Acetophenone	C ₈ H ₈ O	11.92	0.51	11.92	0.39	0.4
Safrole	C ₁₀ H ₁₀ O ₂	16.54	0.95	ND	ND	ND
Vanillin	C ₈ H ₈ O ₃	16.91	1.22	1.65	ND	ND
Dimethyl phthalate	C ₁₀ H ₁₀ O ₄	17.6	5.19	ND	ND	ND
Diethyl phthalate	C ₁₂ H ₁₂ O ₄	19.31	ND	ND	0.17	ND
Pentanoic acid	C ₁₆ H ₃₀ O	19.4	0.64	ND	ND	ND
Alpha-cardinol	C ₁₅ H ₂₆ O	20.21	2.78	ND	ND	ND
Hexanedioic acid	C ₁₄ H ₂₆ O	20.28	ND	0.73	ND	ND
Octadecane	C ₁₈ H ₃₈	20.52	0.61	ND	ND	ND
Tetradecanoic acid	C ₁₄ H ₂₈ O ₂	21.14	1.04	ND	ND	ND
Dibutyl phthalate	C ₁₆ H ₂₂ O ₄	23.25	ND	4.41	6.25	2.61
Bis(2-ethylhexyl) phthalate	C ₂₄ H ₃₈ O ₄	28.31	2.7	1.25	0.93	0.69
Di-n-octyl phthalate	C ₂₄ H ₃₈ O	31.12	1.31	0.1	1.32	ND
Squalene	C ₃₀ H ₅₀	30.37	13.47	1.09	2.05	5.96

Note: ND is "not detected".

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Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interest's statement

The authors declare no competing interests.

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